

## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 Background of Study**

##### **1.1.1 Water Crisis**

Water is vital for all living things and it is an essential element of life. It is fundamental to maintain the integrity and sustainability of the earth's ecosystem. However, the availability and accessibility to freshwater has been proved as one of the most severe case effected in recent years (Chun, 2010).

The UN environmental report GEO 2000 proclaims that “the world water cycle seems unlikely to be able to cope with the demands that will be made of it in the coming decades” where global water crisis express a full scale of emergency (Chun, 2010). Besides, World Wide Fund for Nature (WWF) also stresses on freshwater issue where freshwater is important to human health, agriculture, industry and natural ecosystems. However, freshwater is limited in many regions of the world (Chun, 2010). Based on 1<sup>st</sup> and 2<sup>nd</sup> United Nations World Water Development Reports, 6,000 people in which mainly children under the age of five are dying from water related diseases every day (Chun, 2010). Moreover, more than a billion people lack of safe drinking water (Chun, 2010). These scenario will become more serious unless effective and correct actions are taken. To make matter worst, the limited supply of freshwater has been seriously threated with constant discharge of pollutant which include release of industrial effluent from textile industries.

### 1.1.2 Usage of Dyes in Industry

High level production and usage of dyes worldwide generate coloured water that cause environmental concern. Industries such as textile company, paper and pulp mills, dye manufacturing industries, food companies, electroplating factories and distilleries produced and discharged coloured effluent (Xing *et al.*, 2010). Easton (1995), quoted by Pignon (2006) estimated the industries consume more than 100 tons per year of dyes. It is 90% of the 3,000 compounds registered in the “Colour Index”. Previous study reported approximately 280,000 tons of textile dyes were discharged into the environment per year. Consequently, most of the textile dyes remained in marine ecosystem (Shertate and Thorat, 2013). Table 1.1 shows the loss of dye as effluent after dyeing process for different dye-fiber systems.

Table 1.1: Dye loss as effluent for different dye-fiber systems (Shertate and Thorat, 2013; Chun, 2010).

Dye Class	Fiber	Loss as effluent (%)
Acid	Polyamide	5-20
Basic	Acrylic	0-5
Direct	Cotton	5-30
Disperse	Polyester	0-10
Metal-complex	Wool	2-10
Reactive	Cotton	10-50
Vat	Cotton	5-20
Sulfur	Cellulose	10-40

Malaysian textile and apparel industries has accelerated with about 900 companies throughout the country which employ more than 68,000 workers (Mitchell, 2006). In Malaysia, this industry contributes approximately 2.3% to the country's total exports of manufactured goods and was the 10<sup>th</sup> largest export earner in 2011 (Malaysia Investment Development Authority, 2012).

### **1.1.3 Environmental Impacts of Dyes**

The discharged of coloured effluent impose negative result for both toxicological and esthetical reasons. Aquatic communities are impacted upon dyes effluent release as many dyes are toxic. It also impedes light penetration which upset the biological cycle within the stream and decrease the aesthetic value of the environment. Dyes are recalcitrant organic molecules which are resistant to aerobic digestion and stable to light, heat and oxidizing agents (Chun, 2010). The presence of dyes will light penetration in water which can affect photosynthesis process and hamper aquatic life ecosystem. Besides, breakdown of dye's products might be toxic to some aquatic organisms (Pathiraja, 2014).

Numerous dyes are noticeable in water at concentration as low as 1 mg/L and textile effluent usually contain 10 – 200 mg/L of dye (Pathiraja, 2014). Dyes which are chemically and photolytically stable are highly persistent in natural environment. These two characteristics can cause bioaccumulation of toxic in which may eventually affect human through food chain (Pathiraja, 2014). Hence, it is very crucial to remove dyes from water system.

#### **1.1.4 Methods of Dye Removal**

There are a lot of treatment methods available in order to overcome pollution caused by dye effluent, which includes photocatalytic degradation (Sohrabi and Ghavami, 2008 and Sleiman *et al.*, 2007), sonochemical degradation (Abbasi and Asl, 2008), micellar enhanced ultra-filtration (Zaghbani *et al.*, 2008), cation exchange membranes (Wu *et al.*, 2008), electrochemical degradation (Fan *et al.*, 2008), integrated chemical-biological degradation (Sudarjanto *et al.*, 2006), absorption (Argun, 2010 and Argun and Dursun, 2008) and others. Chemical, biological and physical methods for dye removal are discussed in detail as below.

##### **1.1.4.1 Chemical Methods**

Breakdown of bonds which aid in decolorization and degradation of dyes is the basic step in removing color and toxicity of dyes. Examples of some chemical methods are coagulation, electro-kinetic coagulation, flocculation combined with floatation, electro-flocculation, electrochemical destruction, irradiation, precipitation, oxidation, ozonation and katox treatment (Pathiraja, 2014). However, these techniques can caused secondary pollution as they will generate a huge amount of sludge at the end of the process and creates environmental problems. Moreover, chemical methods will involve high cost, limited versatility, low efficiency and utilize a significant amount of energy. Toxic derivatives such as primary aromatic amines and heavy metals may still present in treated liquor even after the colors are removed by chemical method.

##### **1.1.4.2 Biological Methods**

Biological methods are relatively inexpensive through the use of microorganisms to remove synthetic dyes. The end products of biological methods are fully mineralized through the process of biodegradation (Shertate and Thorat, 2013). The disadvantages

of this method is that they are less flexible in design and operation as they require a large land area and microorganisms are sensitive towards variants. Besides, some of the dyes are resistant to aerobic digestion. The usage of activated sludge for biological treatments do not effectively remove color as the oxidation rate is too low but it can reduce the BOD of the waste water (Pathiraja, 2014).

#### **1.1.4.3 Physical Methods**

Filtration, ion-exchange, membrane filtration and adsorption are some of the example of physical methods for dye removal. Membrane use in filtration need to replace consistently and thus costly with limited life time. The membrane also prone to pore clogging problem. The ion-exchange method enable the solvent to be reclaimed after used with no loss of adsorbent on regeneration. However, this method is not widely used for dye removal treatment as it is not effective in removing all dyes. Unlike the others, adsorption method can remove complete molecules without leaving fragments in wastewater. It is very effective and low in cost (Dotto *et al.*, 2012).

Activation method by using activated carbon is an effective and commercially applicable method to remove dyes in effluent. However, it's wide usage is restricted by the high cost (Xing *et al.*, 2010). Adsorption method is selected for this study to remove basic dyes as it is considered more effective and less expensive as compared to other technologies. It is also well known for its flexibility and simplicity of design, insensitivity to toxic pollutants and the ease of operation (Deans and Dixon, 1992). The most important factor of choosing this method is that it will not produce harmful substances during and after the treatment (Deans and Dixon, 1992).

In recent years, many efforts have been made to study the removal of dye via adsorption using agricultural wastes. Natural materials have potential as low cost adsorbent as they are available in large quantities and environmental friendly. In this study, kenaf, sugarcane bagasse and banana stem were selected to determine their adsorption capability on wastewater of textile industry.

## **1.2 Problem Statement**

Textile industry is very famous in Malaysia. This industry produces wastewater that will contribute to water pollution. Dye removal from textile effluents has been given much attention in the last few years as dye can pose hazards to the environment with the presence of a large number of contaminants, such as toxic organic residues, acids, bases and inorganic contaminants (Ozacar and Sengil, 2003). Some of the dyes were made from hazardous chemicals such as benzidine and metals which are carcinogenic and mutagenic to all form of life (Ozacar and Sengil, 2003).

Dye effluent from textile industries will interfere the transmission of sunlight which will reduce the photosynthetic activity of aquatic life and also affects the aesthetic beauty. This will disturbed the natural equilibrium and affect the aquatic food chain and aquatic life (Hasnain *et al.*, 2007).

Most of the chemical and physical methods used to determine absorbent efficiency are simple in design but the high cost is a disadvantage (Hasnain *et al.*, 2007). Therefore, utilization of agriculture wastes namely kenaf, sugarcane bagasse and banana stem as cheap substitutes can provide a good alternative. These wastes are relatively inexpensive and their reasonable adsorption capacity can be used to remove pollutants such as dye from wastewater effluent.

With this study, it will reduce the pollution intensity of wastewater from textile industry and also identified 'reuse' strategy for agricultural waste of which if not utilized will be send off to landfill for disposal.

### **1.3 Significant of Study**

The result of this research is useful due to the following reasons:

1. It can help the textile industry especially those dealing with dye effluent to treat wastewater more efficiently. Dye in wastewater contains high concentration of pollutants. Due to the low cost of agro-wastes such as kenaf, sugarcane bagasse and banana stem, they can be used as an alternative adsorbent to replace existing commercial adsorbents.
2. This study can give contribution to the existing data on wastewater treatment especially in dye adsorption for future research. Adsorbent is very useful as it can remove the dye from the textile.
3. This research can input useful information on the reuse of agricultural wastes as effective agro-wastes dye adsorbent on related industries.

### **1.4 Objectives of Study**

There are four objectives of this study, which include:

1. To study the adsorption capacity of kenaf, sugarcane bagasse and banana stem.
2. To determine the optimal parameters for efficient dye removal, isotherms and thermodynamics.
3. To calculate and compare the cost of each treatment in determining the most cost-effective application.
4. To determine the calorific value of the adsorbent used.

## **CHAPTER 2**

### **LITERATURE REVIEW**

#### **2.1 Textile Industry in Malaysia**

According to Malaysia Industrial Development Authority (MIDA), textile industry has become the seventh largest contributor of export earnings in manufacturing sector in Malaysia. Malaysia External Trade Development Corporation (Matrade) states that Malaysia produced good quality goods and products include fibers, man-made and natural fiber yarns, woven cotton and man-made fiber fabrics, textile fabrics and related products (Mitchell, 2006).

Malaysian textile industry is very well known for a broad range of activities including polymerization and man-made fiber production, spinning, weaving, knitting, texturizing, dyeing, and printing. Made-up apparel and other textile goods such as home textiles, ropes and carpets, as well as, nonwoven fabrics for personal care, construction, and engineering and furniture applications are also manufactured by most of the Malaysian companies (Mitchell, 2006).

Textile and apparel industry has been foreseen by Third Industrial Master Plan with high forecast of annual growth export of 7.80 % per annum (Lee *et al.*, 2014). Department of Statistics Malaysia has identified that textile and apparel industry in manufacturing sector in year 2012 has contributed 1.70 % to the growth of Gross Domestic Product (GDP) (Department of Statistics Malaysia, 2013). Malaysia's textile and apparel sector has vast experience as a producer of world known brands such as Brooks Brothers, Ralph, Kohl's, Calvin Klein, Alain Delon, Gucci, Polo, Lauren,



Adidas, Nike, Yves St. Laurent, Walt Disney, Reebok, Puma, GAP, Oshkosh, Burberry, Ashworth, etc. (Seong, 2007). Most of the imported markets of Malaysian made textile and apparel are China, Taiwan and Japan while major exported countries are Canada, United States, Turkey and Europe (Seong, 2007). Table 2.1 illustrates Malaysian made textile and apparel.

Table 2.1: Malaysian made textile and apparel.

<b>Textiles</b>	<b>Apparels</b>
Fibres	Overcoats
Yarns (Cotton yarn, CVC yarn, polyester/cotton yarn, polyester/nylon yarn, spun polyester yarn, texturized nylon yarn, polyester filament yarn, acrylic yarn, acrylic/wool blended yarn, worsted and woolen yarn, cotton coarse yarn)	Skirts
Special yarns, textile fabrics and related products	T-shirts
Woven cotton fabrics	Blouses
Fabrics woven of man-made textile materials	Pants undergarments
Knitted or crocheted fabrics	Scarves
Tulles, lace, embroidery, ribbons, trimmings and other small wares	Handkerchiefs
Floor coverings (carpets and rugs)	Headgear (caps and hats)
Home textiles (bed linen, table linen, towels)	Textile accessories (zippers, buttons, sewing thread, industrial thread, embroidered articles, collars, cuffs, hooks and eyes, tape, polyester padding, interlining, Velcro tape, cotton tape and narrow fabric.
Industrial textiles (ropes, cords, car seat fabrics, geo-textiles, dyer fabrics and press belt)	

There are an approximately 1,500 textile factories in Malaysia. High concentration of textile projects is mainly found in the southern region namely Johor. The textile city in Malaysia which is Batu Pahat in Johor locates a total of 40% operating textile factories particularly the wet processing plants. There are 15 out of 40 wet processing plants in

Malaysia situated in Batu Pahat (Malaysian Knitting Manufacturers Association, 1998). The amount of exports of textiles and apparel had increased year to year. Table 2.2 shows Malaysian exports of textiles and apparel by years (Malaysian Knitting Manufacturers Association, 2014).

Table 2.2: Malaysian exports of textiles and apparel by years (Malaysian Knitting Manufacturers Association, 2014).

<b>Year</b>	<b>Textiles (RM Billion)</b>	<b>Apparel (RM Billion)</b>	<b>Total (RM Billion)</b>
1996	3.7	3.3	7.0
1997	4.0	3.6	7.6
1998	4.7	4.9	9.6
1999	4.6	4.9	9.5
2000	5.1	5.3	10.4
2001	4.3	4.7	9.0
2002	4.1	4.5	8.6
2003	4.2	4.3	8.5
2004	5.0	4.6	9.6
2005	5.6	4.7	10.3
2006	6.1	4.8	10.9
2007	5.5	4.8	10.3
2008	5.4	5.1	10.5
2009	5.1	3.8	8.933
2010	5.76	3.565	9.325
2011	6.72	4.09	10.81
2012	5.98	3.48	9.46
2013	6.35	3.91	10.25
2014	6.455	4.57	11.025

According to MATRADE (2013), Malaysian Knitting Manufacturers Association (MKMA), Malaysian Textile Manufacturers Association (MTMA) and Malaysian

Garment Manufacturers Association (MGMA) are three main textile and apparel industry associations in Malaysia. There are a vast range of activities that involved textile and apparel industry. The structure of Malaysian textile and apparel industry is separated into two major sectors which is upstream and downstream by MATRADE (Lee *et al.*, 2014). At the earlier stage, upstream comprises of activities before the manufacturing of textile and apparel, for example, fibre, yarn, fabric, wet, spinning, knitting, weaving, dyeing, printing, silk screening and embroidery processing activities. On the other hand, downstream includes activities after the manufacturing of apparel, textile products, home textiles and clothing accessories (Lee *et al.*, 2014).

One of the main pollution source of textile wastewater in Malaysia is produced from batik industry during dyeing processes. Treatment and removal are hard and difficult to achieve for waste water through processing (Mobarekeh, 2007). There are several batik industries in Selangor which produce and pollute the nearby water sources.

## **2.2 Environmental Aspects**

Industrial sectors can pollute the environment through many ways. A large volume of hazardous effluent are usually generated by industrial activity. Dye stuff manufacturing, dyeing and textile industries discharged wastewater containing a variety of dyes into water bodies. The presence of dyes in water will reduce the light penetration, precluding the photosynthesis of aqueous flora (Paven *et al.*, 2007). Some dyes can cause health problem such as allergy, dermatitis, skin irritation and cancer to human and being mutagenic (Paven *et al.*, 2007).

Incomplete degradation of bacteria will produced toxic amines if dyes are broken down in sediment (Hamdaoui, 2006). Besides, formation of toxic carcinogens is a huge

problem when dyes laden wastewater is directly discharged into the municipal wastewater plants and environment (Hamdaoui, 2006). Table 2.3 shows the processes that produced specific pollutants into our environment.

Table 2.3: Specific pollutants from textile wet processing operations (Eglia, 2007).

Process	Compounds
Desizing	Sizes, enzymes, starch, waxes, ammonia
Scouring	Disinfectants and insecticides residues, NaOH, surfactant, soaps, fats, waxes, pectin, oils, sizes, anti-static agents, spent solvents, enzymes
Bleaching	H <sub>2</sub> O <sub>2</sub> , AOX, sodium silicate or organic stabilizer, high Ph
Mercerizing	High pH, NaOH
Dyeing	Color, metals, salts, surfactants, sulphide, acidity/alkalinity, formaldehyde
Printing	Urea, solvents, colour, metals
Finishing	Resins, waxes, chlorinated compounds, acetate, stearate, spent solvent and softner

Demand in searching for cheaper method of pollutant removal is initiated with the increase in pollution monitoring, controlling and elimination cost. Hence, an economical way of dye removal is more preferable in which sorption process come out to be an effective and attractive treatment process. Sorption process is easy to operate with simple design, less investment in both initial cost and land required, and no consequences of toxic substances and superior removal of organic waste materials (Lee, 2009).

### **2.3 Wastewater Treatment in Textile Industry**

Textile industries have been investigating to find alternatives to reduce harmful substances for mutagenic, carcinogenic and allergic effects of textile chemicals and dyes. There are a large numbers of technologies invented to remove contaminants in effluent (Pereira and Alves, 2012).

Textile wastes can be divided into hard to treat, high dispersible, hazardous and toxic, and large volume waste (Karmakar, 1999). Selection of appropriate treatment method is crucial to overcome the problems caused by textile discharges. The treatment method chosen will be based on factors related to effluent characteristics, including relative costs, level of treatment required and site restriction (Karmakar, 1999).

There are three stages of wastewater treatment in textile industry; primary, secondary and tertiary treatment. Primary treatment consists of physical treatment (equalization, screening and settling) and chemical treatment (neutralization, lime addition, alum addition and iron salt addition). Biological treatment (activated sludge, extended aeration, lagoons) and physical/ chemical treatment (powdered activated carbon addition to biological process) are involved in secondary treatment while in tertiary treatment, physical treatment (secondary clarification, mixed media filtration, granular activated carbon, powdered activated carbon) and chemical treatment (ozonation and chlorination) are involved (Lim, 2011).

## **2.4 Colorant**

Colorants tend to be coloured as they have a characteristic to absorb visible light from 400 to 700 nm. Colorant can be divided into natural organic and inorganic. Although colorants has been used since prehistoric times, the discovery of mauve in 1865 by Perkin which initiated the synthetic dye industry (Yasmin, 2004).

Colorant can be either dyes or pigment. An ideal characteristic of pigments is that they are practically insoluble in the media where they are applied. An additional compound need to be added to the attached pigment particles such as by a polymer in paint, in a plastic or in a melt. However, dyes are only applicable to various substrates from a liquid where they are completely or partially soluble and required to possess specific affinity to the substrate for which they are used (Yasmin, 2004).

## **2.5 Dye**

Dyeing, paper and pulp, textiles, plastics, leather, cosmetics and food industries used dye for a long period of time. The effluent being discharged by these manufacturing and processing industries will pose certain hazards and environmental problems (Pearce, 2003). Dye is a type of colorants which provide a color to the substrate either in the form of aqueous solutions, non-aqueous solution or aqueous suspension. It can be defined by various configurations of unsaturated groups called chromophore groups (Lam, 2005). Chromophore groups is responsible in adsorbing the light of a specific wavelength within the visible light spectrum which results in variety of color that a dye exhibits (Lam, 2005). Figure 2.1 shows some examples of chromophore groups.

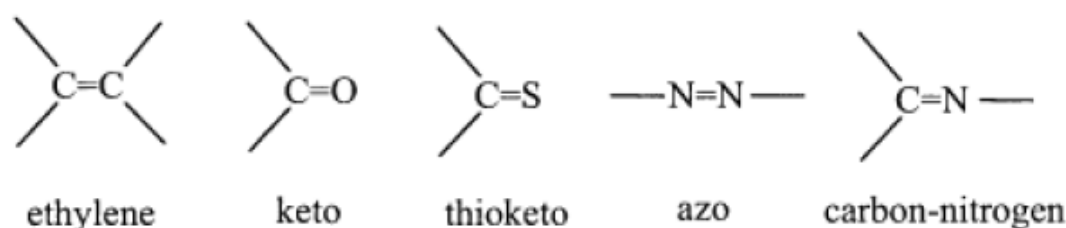


Figure 2.1: Examples of chromophore groups (Lam, 2005).

According to Pearce (2003), textile industry uses dyes and pigments to colour their products and there are more than 100,000 commercially available dyes with over  $7 \times 10^5$  tonnes of dye stuff which are produced annually. Dye is stable and difficult to biodegrade as it has complex aromatic molecular structures. In addition, dyes are harmful to some microorganisms and may cause direct destruction or inhibition in the catalytic capabilities (Pearce, 2003). Direct dye, reactive dye, acid dye and basic dye are dyes that are used in textile industries where all of them may cause acute disease since they are considered as toxicants and carcinogen. It is found that dyes can cause numeral negative impacts in water through several ways:

- Acute or chronic effect on organisms depends on the dye concentration and exposure time.
- Abnormal coloration of subsurface waters as dyes are highly visible.
- Dramatic effect on bacteria's growth and influence on their biological activity as dyes can be absorb or reflect sunlight entering the water.
- Dyes are difficult to treat as they have many different and complicated molecular structures.
- Dyes destroy aquatic life as dyes in wastewater undergo chemical and biological changes and consume dissolved oxygen in stream.

## **2.6 Classification of Dyes**

Today, many new types of dyes have been developed and put into regular use with the invention of synthetic materials used in textiles. Dyes and pigments are two basic methods to color textiles. Pigments are resins which mechanically bound to fibers. Dyeing is most conventionally and commonly used colorization technique.

Dyes can be classified in several ways. Color Index is one of the well-known system of classification that being used internationally. Color Index is devised by the Society of Dyers and Colorists in year of 1924 (Chun, 2010). Dyes can be divided into acid dyes, premetalized acid dyes, chrome dyes (mordant dyes), cationic dyes (basic dyes), direct dyes (substantive dyes), direct developed dyes, disperse dyes, naphthol dyes, reactive dyes, sulfur dyes, and vat dyes according to the types of fibers they are most compatible with (Price *et al.*, 2005).

### **2.6.1 Acid Dyes**

Acid dyes are most suitable for protein fibers, nylon spandex and special type acid dyeable acrylic fibers. Acid dyes can give bright colors with fabulous fastness, ability to stay on the fabric and not to fade and to dry cleaning (Price *et al.*, 2005).

### **2.6.2 Premetalized Acid Dyes**

Some types of fibers are used for both premetalized acid dyes and chrome dyes. Premetalized acid dyes are less bright with better fastness to light and sweat whereas chrome dyes are dull and have excellent fastness to light, washing and perspiration. Both dyes are good for wool and carpets (Price *et al.*, 2005).



### **2.6.3 Mordant Dyes (Chrome Dyes)**

Mordant is a chemical that have affinity for both fiber and dye. It produces dye-mordant-fiber complex and enhances affinity. Mordants are metal salts and are electrically cationic. All mordant dyes are acid dyes but the reverse is false. Mordant dyes improve fastness, promote dye-metal complex formation and boost acid dye uptake due to cationic nature of chromium salts. Mordant dyeing methods are very useful in cottage industries to dye wool with superior wash fastness (Clark, 2011).

### **2.6.4 Cationic Dyes (Basic Dyes)**

Cationic dyes are used for acrylic, modacrylic, cationic dyeable polyester, cationic dyeable nylon, cellulosic, and protein fibers which produce bright colors with bright colors that have excellent fastness to light, laundering, perspiration, and crocking on synthetics fibers (Price *et al.*, 2005). Example of cationic dyes are Methylene Blue, Malachite Green, Gentian Violet and etc.

#### **2.6.4.1 Methylene Blue**

The IUPAC name of methylene blue (MB) is 3,7-bis(Dimethylamino)- phenothiazin-5-ium chloride. Methylene blue is a basic aniline dye with a chemical formula of  $\text{CH}_{18}\text{N}_3\text{SCl}$ . It is a cationic thiazine dye which shows deep blue color in oxidized state but colorless in reduced form, leukomethylene blue (LMB) (Cragan, 1999). It inhibits guanylate cyclase and has been used to treat cyanide poisoning and to lower levels of methemoglobin. Methylene blue can be used as a bacteriologic stain and as an indicator. It is also used in coloring paper, temporary hair coloring, dyeing cotton and wools, and coloring of paper stocks (Han, 2007). Methylene blue will dissociate in aqueous solution into methylene blue cation and chloride ion. The serious consequences from methylene blue contamination to human and the environment urge the need to remove

methylene blue from any wastewater (Altaher *et al.*, 2011). The cation  $C_{16}H_{18}N_3S^+$  is present in the methylene blue structure. The closest ion to the methyl group which is the chloride ion suggests a distribution of charge between the terminals of amine group to form a stable structure of methylene blue (Cragan, 1999). Figure 2.2 shows the structure of methylene blue.

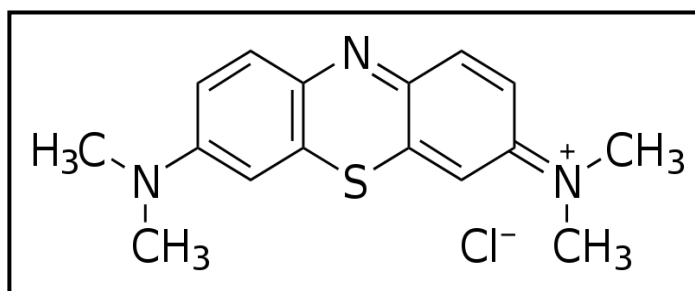


Figure 2.2: Structure of methylene blue (Cragan, 1999).

#### 2.6.5 Direct Dyes (Substantive Dyes)

Direct dyes are generally used on cellulosic fibers. They are excellent fastness to perspiration and dry cleaning. Direct developed dyes are good as fastness to laundering. They can apply on same cellulosic fibers (Price *et al.*, 2005).

#### 2.6.6 Disperse Dyes

Disperse dyes can be used for acetate, acrylic, modacrylic, nylon, polyester, and olefin fibers. The wash fastness with disperse dyes differ with the types of fibers used. It is good on polyester but poor on acetate. Disperse dyes are good in fastness for perspiration, crocking, and dry-cleaning (Price *et al.*, 2005).

### **2.6.7 Naphthol Dyes**

Naphthol dyes create bright shades of color with varying fastness to light for cellulosic fibers. They have good fastness to washing and perspiration (Price *et al.*, 2005).

### **2.6.8 Reactive Dyes**

Reactive dyes are employed for cellulosic fibers but occasionally on protein fibers and nylon as well. They can give bright shades with excellent fastness in all areas but they are difficult to match shades (Price *et al.*, 2005).

### **2.6.9 Sulfur Dyes**

Sulfur dyes are utilized for cellulosic fibers and create dull shades such as navy, black, and brown. They are weak when exposed to chlorine but excellent fastness in most area (Price *et al.*, 2005).

### **2.6.10 Vat Dyes**

Vat dyes if not properly applied may crock. Vat dyes have fabulous fastness in all areas especially to chlorine and bleach. They are used on cellulose material (Price *et al.*, 2005).

Color Index will divide dyes by referring each dye a generic name determined by its application characteristics. Then, a Color Index constitution number will be referred to the dyes based on its chemical structure if known (Lam, 2005). Dye classes, substrates, method of application and chemical types are summarized in Table 2.4.

Table 2.4: Application classes of dyes and their chemical types (Chun, 2010).

Classes of dye	Substrates	Method of application	Chemical types
Acid	Nylon, wool, silk, paper, inks and leather	Usually from neutral to acidic dye baths	Azo including premetalized anthraquinone, triphenylmethane, azine, xanthene, nitro and nitroso
Azoic components and compositions	Cotton, rayon, cellulose acetate and polyester	Fiber impregnated with coupling component and treated with a solution of stabilized diazonium salt	Azo
Basic	Paper, polyacrylonitrile-modified nylon, polyester and inks	Applied from acidic dye baths	Diazacarbocyanine, cyanine, hemicyanine, diazahemicyanine, azo, azine, xanthene, acridine, oxazine and anthraquinone
Direct	Cotton, rayon, paper, leather and nylon	Applied from neutral or slightly alkaline baths containing additional electrolyte	Azo, phthalocyanine, stilbene and oxazine
Disperse	Polyester, polyamide, acetate, acrylic and plastics	Fine aqueous dispersions often applied by high temperature-pressure or lower temperature carrier methods; dye may be padded on cloth and baked on or thermofixed	Azo, anthraquinone, stryl, nitro and benzodifuranone
Fluorescent brighteners	Soap and detergents, all fibers, oils, paints and plastics	From solution, dispersion or suspension in a mass	Stilbene, pryrazoles, coumarin and naphthalimides
Food, drug and cosmetic	Foods, drugs and cosmetics		Azo, anthraquinone, carotenoid and triarylmethane
Mordant	Wool, leather and anodized	Applied in conjunction with cleaning Cr salts	Azo and anthraquinone
Natural	Food	Applied as mordant, vat, solvent or direct and acid dyes	Anthraquinone, flavonols, flavones, indigoids, chroman
Oxidation bases	Hair, fur and cotton	Aromatic amines and phenols oxidized on the substrate	Aniline black and indeterminate structure

Table 2.4: Application classes of dyes and their chemical types (Chun, 2010)  
(Continued).

Reactive	Cotton, wool, silk and nylon	Reactive site on dye reacts with functional group on fiber to bind dye covalently under influence of heat and pH (alkaline)	Azo, anthraquinone, phthalocyanine, formazan, oxazine and basic
Solvent	Plastics, gasoline, varnish, lacquer, stains, inks, fats, oils and waxes	Dissolution in the substrate	Azo, triphenylmethane, anthraquinone and phthalocyanine
Sulfur	Cotton and rayon	Aromatic substrate vatted with sodium sulfide and re-oxidized to insoluble sulfur containing products on fiber	Indeterminate structure
Vat	Cotton, rayon and wool	Water insoluble dyes solubilized by reducing with sodium hydrosulfite, then exhausted on fiber and re-oxidized	Anthraquinone (including polycyclic quinones) and indigoids
Pigments	Paints, inks, plastics and textiles	Printing on the fiber with resin binder or dispersion in the mass	Azo, basic, phthalocyanine, quinacridone and indigoid

## 2.7 Existing Approaches of Dye Removal

Many conventional methods in treating dye effluent is not widely applied and practiced in a large scale in paper and textile industry due to its high cost and disposal problem. They aim to treat effluent or waste stream so it would be suitable and environmental friendly for reuse. Physical and chemical treatments are more favorable in treating industrial effluent as industrial wastewater often consist of pollutants that cannot be removed efficiently by microorganism (Lee, 2009).

### **2.7.1 Biodegradation**

Biodegradation is the most cost effective treatment as compared to other physical and chemical processes. Examples of biodegradation methods are fungal decolourization, microbial degradation, adsorption by living or dead microbial biomass and bioremediation system. Microorganisms such as bacteria, fungi, yeasts and algae are capable to accumulate and degrade different pollutants (Lee, 2006).

Biological treatment are often restricted due to its technical constraints. Some of the organic molecules are recalcitrant because of their complex chemical structure and synthetic organic origin. Besides, this technique uses a large land area and it is restricted by sensitivity toward diurnal variation with the toxicity of some chemicals and less flexibility in design and operation (Crini, 2006).

### **2.7.2 Coagulation – Flocculation**

Coagulation transform finely divided suspension of solid into larger particles to enable settling process (Lee, 2006). Further collisions between the particles formed by coagulation by mixing process which results in the formation of relatively large particles that can be removed easily. It is termed as flocculation (Binnie *et al.*, 2002).

Coagulation happens quickly while flocculation is the term applied indicating a longer process of forming larger particles via the process of coagulation. Coagulant is a chemical that is dosed to cause particles to coagulate (Binnie *et al.*, 2002). Alum, ferric chloride, ferric sulfate, sodium aluminate and various cationic polymers are common coagulants used in conventional water treatment (Pizzi, 2011). Figure 2.3 showed the physical-chemical process involved in coagulation-flocculation.

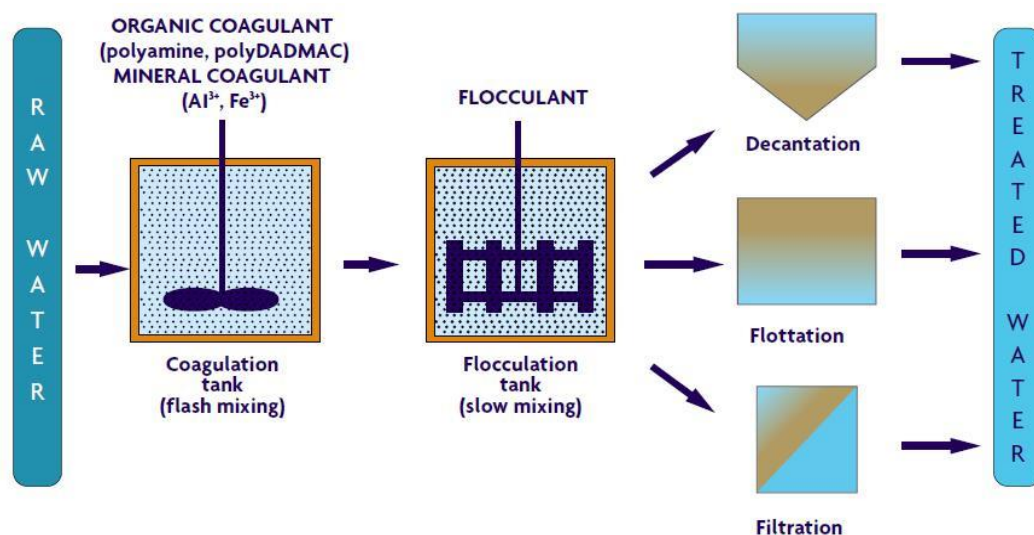


Figure 2.3: Coagulation-flocculation process.

### 2.7.3 Adsorption by Activated Carbon

Activated carbon is defined as amorphous carbon-based materials that have an extended interparticulate surface area and high degree of porosity (Bansal and Goyal, 2005). Activated carbon are used widely in many areas especially in the environmental field. Liquid phase applications include purification in the clothing, textile, pharmaceutical industries, food processing, preparation of alcoholic beverages, decolourization of oils and fats, product purification in sugar refining, purification of chemicals (acids, amines, glycerine, glycol, etc.), enzyme purification, decaffeination of coffee, gold recovery, refining liquid fuels, purification of electroplating operations, personal care, cosmetics and application in the chemical and petrochemical industries (Cecen and Aktas, 2011). Among the gas phase applications are recovery of organic solvents, removal of sulphur-containing toxic components from exhaust gases and recovery of sulphur, biogas purification, use in gas masks and others (Cecen and Aktas, 2011). It also contributes in medical and veterinary application, soil improvement, removal of pesticide residues and nuclear and vacuum technologies (Cecen and Aktas, 2011).

Activated carbon can be produced from combustion, partial combustion or thermal decomposition of a number of carbonaceous substances. It can be obtained in granular and powdered forms. Nowadays, they are created in spherical, fibrous and cloth forms for some special applications (Bansal and Goyal, 2005). Granular form of activated carbon possessed larger internal surface area and smaller pores, and the finely divided powdered form come with large pore diameters and a smaller internal surface area. Activated carbon fibres and carbon cloth contain comparatively high coverage of larger pores and have a larger surface area (Bansal and Goyal, 2005).

Adsorption of activated carbon is generally applied in industrial wastewater treatment plant to comply stringent regulations for effluent discharged to receiving water. Activated carbon adsorption can apply as a separate unit process (Bansal and Goyal, 2005). It can be installed after several physiochemical treatment steps, for example, coagulation/clarification, filtration and dissolved air flotation. Another preference is to place activated carbon adsorption prior to biological treatment (Cecen and Aktas, 2011). Almost 300,000 tons/year (nearly 80%) of the total active carbon is consumed for liquid-phase applications and about 20% of the total production of active carbon is used in gas phase application (Bansal and Goyal, 2005). Figure 2.4 showed the different forms of activated carbon.



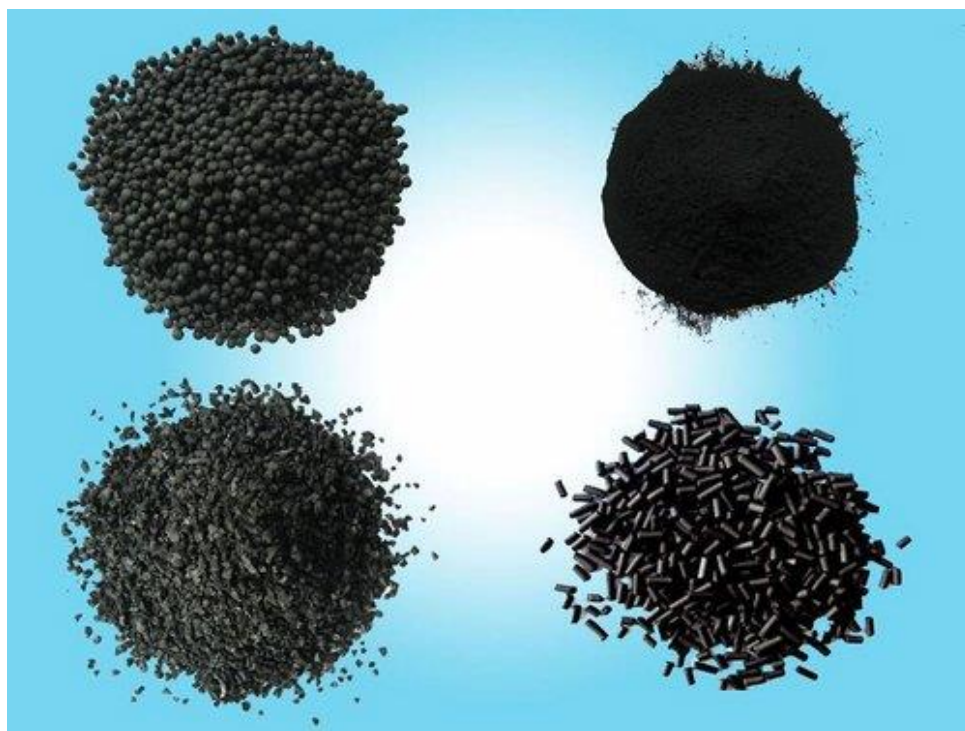


Figure 2.4: Activated carbon in different forms.

#### 2.7.4 Ozone Treatment

Ozone is an excellent oxidizing agent (oxidizing potential, 2.07) as compared to chlorine (oxidation potential, 1.36) and  $\text{H}_2\text{O}_2$  (oxidizing potential, 1.78) which pioneered used in early of 1970s. Oxidation by ozone can degrade chlorinated hydrocarbons, phenols, pesticides and aromatic hydrocarbons. Total colour and residual COD with no residue or sludge formation and no toxic metabolites are the two variables that should to be considered on deciding the amount of dosage of ozone required to be applied to the dye containing effluent. This method favours double bonded dye molecules. One of the significant advantages of this treatment method is that ozone can be applied in gaseous state and hence it does not raise the volume of wastewater and sludge (Robinson *et al.*, 2001).

Chromophore groups in the dyes are basically organic compounds with conjugated double bonds that can be broken down into smaller molecules in which reduce in colouration. Carcinogenic or toxic properties of these smaller molecules might increase and therefore, ozonation may be used alongside a physical method to hamper this (Robinson *et al.*, 2001). Decolouration can occur in a relatively short time (Robinson *et al.*, 2001).

The detriment of having ozone treatment is its short half-life (typically being 20 minutes) (Robinson *et al.*, 2001). With the present of dye, the time will be further shortened as the stability is affected by the presence of salts, pH and temperature (Robinson *et al.*, 2001). Ozone depletion will accelerate in alkaline conditions, thus, careful monitoring of the effluent pH is a compulsory (Robinson *et al.*, 2001). Irradiation or a membrane filtration technique can be improvised to improve the result (Robinson *et al.*, 2001). Ozone treatment requires an extensive high cost as continuous ozonation is required due to its short half-life (Robinson *et al.*, 2001). Figure 2.5 showed an ozone treatment process.

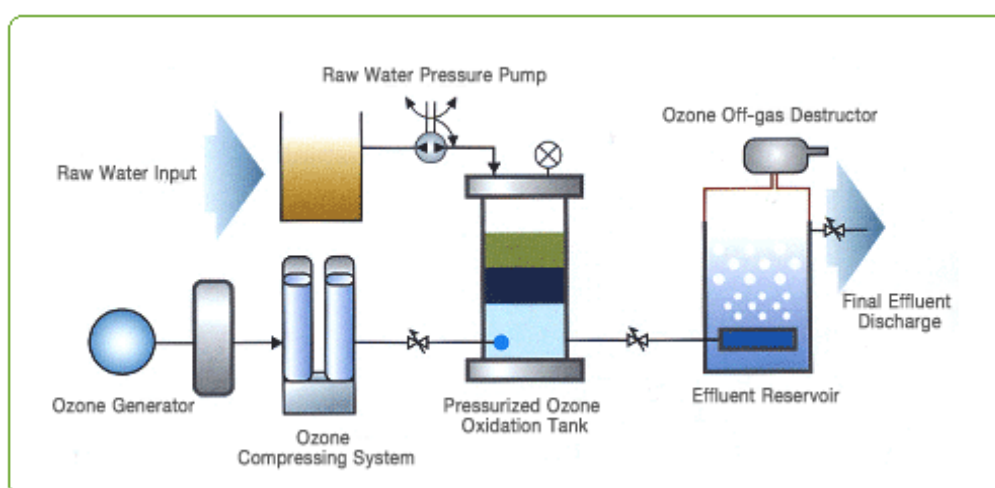


Figure 2.5: Ozone treatment process.

### **2.7.5 Electrochemical Processes**

This technique is developed in mid 1990s. It has been proved to be an effective method for dye removal as it required little or no chemicals and no sludge formation. This technique proves to have no hazardous breakdown metabolites leaving the treated wastewater safe to be released back into the water body. It is an economically feasible method with high efficiency in removing and degrading dyes of recalcitrant pollutants. The cost of electricity used is comparable to the price of the chemicals (Robinson *et al.*, 2001). The relatively high flow rates cause a direct decrease in dye removal (Robinson *et al.*, 2001).

### **2.7.6 Reverse Osmosis**

Reverse osmosis (RO) is a membrane-based demineralization technique. The main function of reverse osmosis is to isolate dissolved solids such as ions from aqueous solution. Membrane is used in this technique worked as a permeable selective barrier that enable some species to selectively permeate through and selectively retaining other dissolved species (Kucera, 2011). Reverse osmosis is believed to remove hardness, colour, many kinds of bacteria and viruses, and organic contaminants (Abid *et al.*, 2012). Nataraj *et al.* (2009) and Abid *et al.* (2012) had successfully proved that reverse osmosis can efficiently remove dye substances from water body. The water produced by reverse osmosis can be recycled since it is close to pure water (Gupta and Suhas, 2009). Figure 2.6 illustrated the key components in reverse osmosis membrane.

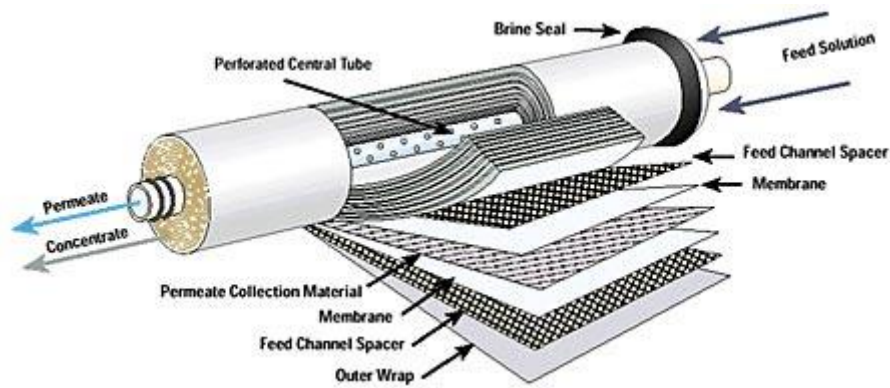


Figure 2.6: Components of reverse osmosis membrane.

### 2.7.7 Nanofiltration

Nanofiltration possess approximately 0.0012 - 0.012  $\mu\text{m}$  of pore size for particles and molecules separation with a pressure range of 20 – 40 bar. The dissociation of surface functional groups or adsorption of charge solute caused nanofiltration's membranes in contact with aqueous solution to be slightly charged. Nanofiltration's membrane is very useful in separating inorganic salts and small organic molecules. Its properties of low rejection of monovalent ions, high rejection of divalent ions and higher flux enabled it to be applied in many areas especially for water and wastewater treatment, pharmaceutical and biotechnology and food engineering (Mohammad, *et al.*, 2014).

Fundamental factors that affect the performance of the membranes are membrane material (charge of the membrane) (Nada, 2014). Charge synergy plays a role due to the dimension of pores which are less than one order of magnitude larger than the size of ions used to separate ions with different valences (mainly bivalent ions) (Nada, 2014). The concentration of polymers, presence and concentration of additives, and temperature of the polymers (solution) during fabrication, are three major parameters that might affect the performance and morphology of nanofiltration membranes (Nada, 2014). Figure 2.7 showed the types of materials that nanofiltration can filter.

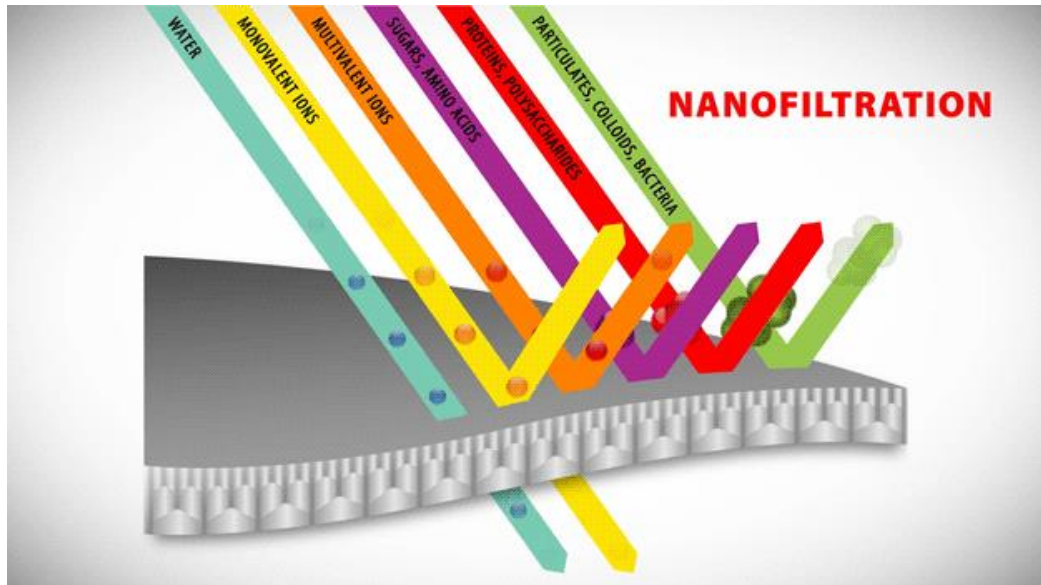


Figure 2.7: Types of materials that can be filtered by nanofiltration.

### 2.7.8 Ultrafiltration – Microfiltration

Ultrafiltration and microfiltration membranes allow particles transportation to occur at their distinct and permanent porous network. These two membranes are unable to reveal intrinsic properties of the polymeric materials and the intrinsic selectivity for the transport species as compared with nonporous membranes (Lawrence *et al.*, 2010).

Both ultrafiltration and microfiltration are classified as low-pressure membranes with larger pore sizes used for the purpose of filtration. Low-pressure membranes focus on physical removal process where the size of the pores justify what contaminants can be removed from the process. Ultrafiltration membranes can filter a portion of fine particles that could pass through microfiltration membranes. One of the disadvantages of ultrafiltration and microfiltration is both membranes are unable to remove dissolved substances (AWWWA Staff, 2011).

### **2.7.9 Ion Exchange**

Ion exchange is used in removing cationic and anionic dyes. Wastewater with dye will pass through the ion exchange resin until the vacant exchange sites are saturated (Chun, 2010). Ion exchange resins contain either organic or inorganic network structure with attached functional groups (Eckenfelder *et al.*, 2009). Synthetic resins made by polymerization of organic compounds are used by most ion exchange resins in wastewater treatment. They are usually made into porous three dimensional structure. Ion exchange resins are anionic if they switch negative ions and cationic if they switch positive ions. The disadvantages of this method are it cannot accommodate a wide range of dyes (Chun, 2010) and the usage of expensive solvents for regeneration of the ion exchanger.

### **2.7.10 Fenton's Reagent ( $\text{H}_2\text{O}_2\text{-Fe}^{2+}$ salts) Treatment**

Fenton's reagent (hydrogen peroxide activated with  $\text{Fe}^{2+}$  salts) treatment is a chemical process benefits in treating wastewater that are resistant to biological treatment or are hazards to live biomass. This treatment has high efficiency on organics oxidation as the result of the generation of the hydroxyl radicals (Lam, 2005). Hydroxyl radicals will abstract protons to produce organic radical compounds in order to degrade organics. Those organic radical compounds are subject to further oxidation and are very reactive (Chun, 2010). This treatment is best in COD, color and toxicity reduction. However, this method will result in sludge generation via the flocculation of the reagent and the dye molecules. The sludge need to have further disposal option.

### **2.7.11 Photochemical (H<sub>2</sub>O<sub>2</sub>-UV radiation)**

The end products of this treatment are CO<sub>2</sub> and H<sub>2</sub>O via dye molecules degradation by UV treatment in the presence of H<sub>2</sub>O<sub>2</sub> (Chun, 2010). Chemical oxidation of organic materials will occur as ultraviolet light invades causes dissociation of hydrogen peroxide into hydroxyl radicals. Ultraviolet light solely has the capability to degrade organic compounds but the combination of ultraviolet light and hydrogen peroxide has the potential to far more enhance the overall oxidation process (Chun, 2010).

### **2.7.12 Photocatalytical (TiO<sub>2</sub>-UV radiation)**

Titania is a photocatalyst broadly used for generating charge carriers that induced reductive and oxidative processes (Gaya and Abdullah, 2008). Electrons are shifted from the valence band to the conduction band of the TiO<sub>2</sub> particle cut out positively charged holes when the surface of TiO<sub>2</sub> particles in anatase form is exposed to UV light. Dye pollutants can be oxidized by the photogenerated holes directly through the valence band hole before it is captured either within the particle or at the surface of the particle or circumlocutorily through the surface bound hydroxyl radical (i.e., a trapped hole at the particle surface) (Chun, 2010). The photogenerated electrons can trigger the reductive decolourization of dyes (Chun, 2010). The disadvantages of this method include the final products of photocatalytic degradation may not be purely innocuous substances and may not have complete redox reactions with the electron hole recombination process (Gaya and Abdullah, 2008). *Escherichiacoli* proclaimed that nano-scale TiO<sub>2</sub> water suspension is toxic. However, there has been limited research on the toxicity of the photocatalyst or the complete photocatalytic process.

There are various types of wastewater treatments used in textile industry. It is based on the types of pollutants that need to be treated. Table 2.5 shows the advantages and disadvantages of various types wastewater treatment used in textile industry.

Table 2.5: Advantages and disadvantages of different wastewater treatment used in textile industry.

Processes	Advantages	Disadvantages	References
Biodegradation	Rates of elimination by oxidizable substances about 90%	Low biodegradability of Dyes	Pala and Tokat, 2002; Ledakowicz <i>et al.</i> , 2001.
Coagulation–Flocculation	Elimination of insoluble dyes	Production of sludge blocking filter	Gaehr <i>et al.</i> , 1994.
Adsorption on activated carbon	Suspended solids and organic substances well reduced	Cost of activated carbon	Arslan <i>et al.</i> , 2000.
Ozone treatment	Good decolorization	No reduction of the COD	Adams <i>et al.</i> , 1995. .
Electrochemical Processes	Capacity of adaptation to different volumes and pollution loads	Iron hydroxide sludge	Lin and Chen, 1997.
Reverse osmosis	Removal of all mineral salts, hydrolyzes reactive dyes and chemical auxiliaries	High pressure	Ghayeni <i>et al.</i> , 1998.
Nanofiltration	Separation of organic compounds of low molecular weight and divalent ions from monovalent salts.	-----	Akbari <i>et al.</i> , 2002. .
Ultrafiltration–Microfiltration	Low pressure	Insufficient quality of the treated wastewater	Ciardelli and Ranieri, 2001



## 2.8 Adsorption

Kayser first recommended the use the term “adsorption” in 1881 to characterize the condensation of gases on free surfaces which is a phenomenon identified independently by both Scheele in 1773 and Fontana in 1777 (Chun, 2010). Adsorption, similar to surface tension, is a consequence of surface energy that is commonly used to remove substances from liquid phases (gases or liquids). It is also a natural phenomenon that enrich chemical species from a liquid phase on the surface of a liquid or a solid.

Adsorption is capable in removing molecules or ions from aqueous solution and in water treatment field, adsorption has been proved powerful in the removal process for multiple solutes (Worch, 2012). If the concentration of the species in the fluid-solid boundary is larger than that in the bulk of the fluid, a species exist in the fluid phase is consider to be adsorbed on the solid surface (Chun, 2010). Adsorbate is the species that is adsorbed. There can be one or more adsorbates in a given adsorption situation. Adsorbent is the solid substance upon whose surfaces adsorption take place.

Major characteristic of solid surfaces are its active and energy-rich sites. Those characteristics enable interaction with solutes in the adjacent aqueous phase by their specific electronic and spatial properties (Worch, 2012). Generally, active sites have different energies where the surface is energetically heterogeneous (Worch, 2012).

Basic terms of adsorption theory is illustrated in Figure 2.8. Adsorbent is referred as the solid material that serves the surface for adsorption; adsorbate is the species that will be adsorbed (Worch, 2012). Adsorbed species can be released and transferred back from the surface into the liquid phase by changing the properties of the liquid phase, for

example, concentration, pH and temperature (Worch, 2012). The term of this reverse process is desorption (Worch, 2012).

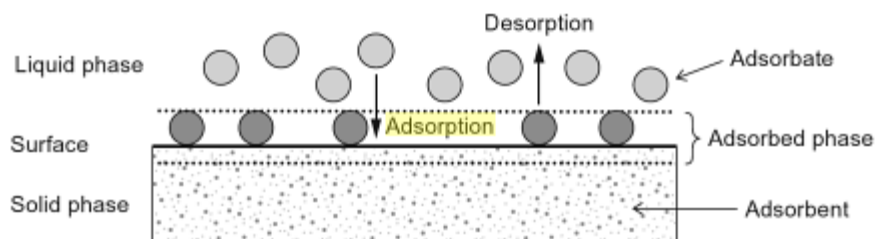


Figure 2.8: Basic process of adsorption (Worch, 2012).

All adsorption processes can be divided into two categories of physical and chemical adsorption rely upon the strength of the interaction (Lowell *et al.*, 2004). Characteristic of the adsorbate-adsorbent system is the extend of the adsorption of an adsorbate on an adsorbent accomplished under a set of conditions. Characteristics of the adsorbate-adsorbent system also influences by the manner of the adsorbate and adsorbent come into contact with each other. Different chemical species may show diverse adsorptive affinity conductive to a particular adsorbent provides the basis of separating or removing these species from their mixtures by applying this adsorbent.

### 2.8.1 Physisorption

Physisorption is defined as physical adsorption in which adsorbate adheres to the surface through weak intermolecular interactions. Physisorption is commonly considered as an efficient way to rapidly lower the concentration of dissolved dyes in an effluent (Sharifah, 2006).

It is characterized by the:

- a) Low temperature, always under the critical temperature of the adsorbate
- b) Type of interaction: Intermolecular forces, dipole-dipole interactions, dispersion forces, induction forces (Van der Waals forces)
- c) Low enthalpy:  $\Delta H < 20$  KJ/mol
- d) Adsorption takes place in multilayer, and
- e) Low activation energy

### 2.8.2 Chemisorption

Chemisorption is related to the chemical reactions between the adsorbate and the surface sites (Worch, 2012). According to Sharifah (2006), it is characterized to have:

- a) High temperature
- b) Type of interaction: Strong; covalent bond between adsorbate and surface
- c) High enthalpy:  $\Delta H \sim 400$  KJ/mol
- d) Adsorption takes place in monolayer
- e) High activation energy

Table 2.6 shows the comparison between physisorption and chemisorption.

Table 2.6: Comparison between physical and chemical adsorption (Sharifah, 2006).

<b>Physisorption</b>	<b>Chemisorption</b>
Molecular condensation in the capillaries.	Monomolecular layer on the surface.
Without chemical bonding.	With chemical bonding.
Reversible can be desorption.	Non-reversible.
Nonselective surface attachment.	Selective surface attachment.

### **2.8.3 Adsorbent**

Adsorbent can be used to define the changes between molecules in a mixture through analysis of adsorption equilibrium and kinetics (Sharifah, 2006). Adsorbent is porous in nature with high surface area that enable adsorption of substances onto its surface by intermolecular forces (Sharifah, 2006).

A solid with fast kinetics but low adsorption capacity and a solid with high adsorption capacity but slow kinetics are both not favorable. Slow kinetics will cause adsorbate molecules to use longer time to reach the particle interior which results in longer residence time in a column and thus low throughput. On the other hand, low adsorption capacity means a huge amount of solid is necessary to attain a given throughput. In short, an effective adsorbent possess great adsorptive capacity by having adequate surface area on a per-unit-mass (or volume) basis and has broad pore network for transfer of adsorbate molecule diffusion which provides good kinetics (Chun, 2010).

Adsorbents such as activated carbon, peat and chitin. have been examined on its possibility to remove dye from aqueous solutions (Sharifah, 2006). Activated carbon has been used widely with a great success in term of adsorption. Activated carbon is popular with high capability of dye removal especially for the adsorption of organic species (Sharifah, 2006). They are widely used for the purpose of unwanted odor, color, taste and other organic and inorganic impurities from industrial and domestic wastewater, solvent recovery, air purification and pollution control plus a variety of gas-phase applications (Bansal and Goyal, 2005). However, due to the high cost production and regeneration of activated carbon, many other resources were investigated on their respective adsorption capability on aqueous solution (Sharifah, 2006).

Commercial types of adsorbents also include silica gel, activated alumina and zeolite. Silica gel and activated alumina are usually used as desiccants and modified form of silica gel and activated alumina are mainly used for special purification process (Yang, 2003). Zeolite, notably synthetic zeolite is another vital class of solid used as broadly as activated carbon. Since they have unique surface chemistries and crystalline pore structure, they are primarily used as adsorbents (Yang, 2003).

#### **2.8.4 Adsorption Mechanism**

Partitioning, Van der Waals forces, electrostatic interactions, hydrogen bonding and hydrophobic interactions are physical binding and physical interactions involved in adsorption process. Figure 2.9 showed the mechanism of adsorption. According to Sharifah (2006), adsorption process can be divided into three steps as follows:

1. Molecule diffusion process into the thin layer of fluid (called as fluid film) which is attached on the adsorbent.
2. According to developing of diffusion, the surface diffusion process which attached the vapour or gas along the pores. It is called as mixed diffusion because there exist two diffusion of pore diffusion and surface diffusion. The bulk adsorption occurs within the pores of adsorbent where the major available surface area is available. Hence, the adsorbate will migrate from the external surface area into the pores within each adsorbent particle.
3. Adsorption process in the pore adsorption sites.

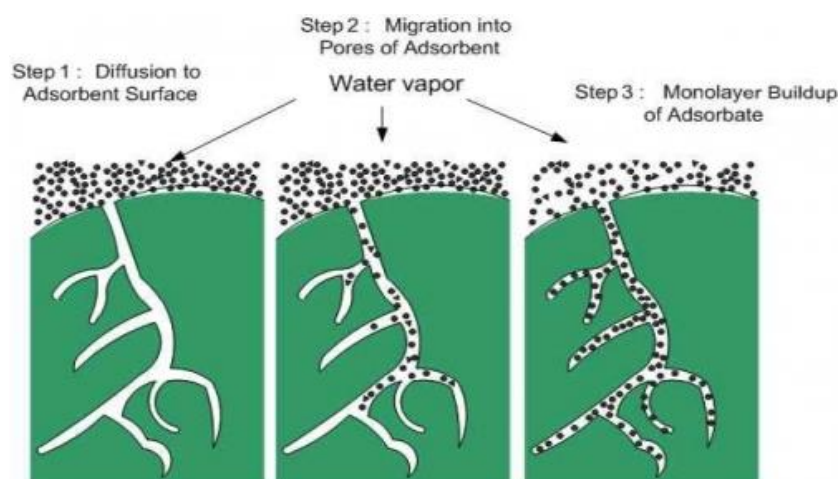


Figure 2.9: Mechanism of adsorption (Sharifah, 2006).

External diffusion, internal diffusion or mixed diffusion (internal diffusion and external diffusion) regulate the rate of adsorption. The function of external diffusion is to regulate the migration of solute species from solution to the boundary layer of the liquid phase. On the other hand, internal diffusion is responsible in controlling the transfer of solute species from external surface of the adsorbent to the internal surface of the adsorbent material. The rate will be governed by particle diffusion if the external diffusion is greater than internal diffusion. A condition may cause molecules to desorb after adsorption. Sometime, adsorbed molecules will react with active sites on the adsorbent pore surfaces and form chemical bonds (Pathiraja, 2014).

Based on Rangabhashiyam *et al.* (2013), dyes adsorption can be explained as:

1. The dye transfer from the bulk solution to the adsorbent surface.
2. Adsorption on the dye surface.
3. Transport within the adsorbent particle.

Kinetics and isotherms data are crucial to interpret the adsorption process as they will present the adsorption mechanism, for example, the bounding of dye within the adsorbent. There are many factors that can affect the adsorption mechanism such as pH, chemical structures, salt concentration and the present of ligands (Rangabhashiyam *et al.*, 2013).

It have been investigated that basic dyes have higher adsorption capacity than acid dyes due to the ionic charges on basic dyes (Rangabhashiyam *et al.*, 2013). Chemical reaction by using covalent bond formation between the dye molecule and fiber makes reactive dyes attach to the adsorbent (Rangabhashiyam *et al.*, 2013). Film diffusion, pore diffusion and intra-particle transport are the three main steps involved in the adsorption mechanism of adsorbate onto adsorbent (Rangabhashiyam *et al.*, 2013). In batch reactor, pore diffusion and intra-particle diffusion are the factors that limit the rate of diffusion (Rangabhashiyam *et al.*, 2013). However, film diffusion is the limiting factor for diffusion in the case of continuous flow system (Rangabhashiyam *et al.*, 2013).

### **2.8.5 Factors Affecting Adsorption**

There are several crucial factors affecting adsorption process, such as:

- i. Surface area of adsorbent

Larger sizes imply a greater adsorption capacity as the amount of surface area increases (Sharifah, 2006).

ii. Contact time / residence time

A complete adsorption can be achieved with a longer contact time (Njoku *et al.*, 2014). At the initial stage of the adsorption process, a higher percentage of textile dyes removal is achieved. Adsorption capability decreases with increasing shaking time until an equilibrium is achieved.

iii. Particle size of adsorbent

Internal diffusion and mass transfer limitation to the penetration of the adsorbate inside the adsorbent can be lowered by having a small particle sizes (i. e. Adsorption capability can be sustained and equilibrium can be easily achieved) (Sharifah, 2006).

iv. Solubility of solute (adsorbate) in liquid (wastewater)

Less soluble substances are more easily and quickly removed from water body (i. e. adsorbate) than substances with high solubility. Non-polar substances are more favorable to remove from aqueous solution than polar substances since latter have better affinity for water (Sharifah, 2006).

v. Degree of ionization of the adsorbate molecule

As compared to neutral molecules, highly ionized molecules are adsorbed in smaller degree (Sharifah, 2006).



vi. pH

pH is one of the most crucial factors that need to be considered as it will affect the capacity of adsorbent in wastewater treatment. Different pH leads to different level of ionization of the adsorptive molecules and the surface properties of the adsorbent (Yagub *et al*, 2014).

vii. Numbers of carbon atoms

A huge amount of carbon atoms is generally associated with a lower polarity for substances in the same homologous series as a higher potential for being adsorbed will be favored (Sharifah, 2006).

viii. Size of molecule with respect to size of the pores

Large molecules size are not able to enter small pores. This will decrease the ability of adsorption independently of other causes (Sharifah, 2006).

ix. Temperature

Temperature is another important physico-chemical process parameter as it will alter the adsorption capacity of adsorbent. The adsorption is an endothermic process if the amount of adsorption increases with increasing temperature. This is because the mobility of the dye molecules increases and the number of active sites available for adsorption increases with increasing temperature (Yagub *et al.*, 2014). The adsorption is exothermic process when there is a decrease of adsorption capacity with increasing temperature. This occurs as the adsorptive forces between the dye species and the active sites on the adsorbent surface decreases as temperature increases result with the decrease in adsorption (Yagub *et al.*, 2014).

## **2.9 Adsorption using Agricultural Waste Products**

### **2.9.1 Characteristics of Agricultural Wastes as Adsorbents**

Numerous amount of agricultural and wood wastes have been used as adsorbents. For example, coir pith, bagasse, silk cotton hull, sago waste, date piths, banana pith, corn cob, straw, maize cob, rice husk, rice hulls, fruit stones, nutshells, pinewood, sawdust, coconut tree dust, bamboo and cassava peel (Rangabhashiyam *et al.*, 2013). Based on physico-chemical characteristics and the cost of agricultural solid wastes, they are good impending adsorbents (Rangabhashiyam *et al.*, 2013).

Hemicelluloses, cellulose and lignin are three main components of agricultural solid wastes (Rangabhashiyam *et al.*, 2013). They have high molecular weights and the extractives is small in molecular size and available in small quantity. Generally, lignocellulosics is termed as biomass. Lignocellulosic materials are a result of photosynthesis, hence, they also called as photo mass (Rangabhashiyam *et al.*, 2013).

Cellulose is an important pure organic polymer composed of anhydroglucose bound together in a large straight chain molecule (Rangabhashiyam *et al.*, 2013). A microfibril is formed as bundles of linear cellulose chains which are combined and oriented in the cell wall structure. Cellulose is insoluble in most of the solvents in nature. It also proved to have low approachability to acid and enzymatic hydrolysis (Rangabhashiyam *et al.*, 2013).

Hemicellulose is a short molecular chain made up of several monosaccharide units. Hemicellulose is partially soluble in water as the polymer chains consists of short branches and are amorphous. The chains of pentose sugar in hemicelluloses serve as the cement material in order to bind the cellulose micells and fiber together

(Rangabhashiyam *et al.*, 2013). Hemicelluloses are easily hydrolyzed and they are highly soluble in alkali (Rangabhashiyam *et al.*, 2013).

Lignins are aromatic compounds. They provides the sealing of water conducting system that links roots with leaves and prevent the plant from degradation. Lignins also gives structural strength to the plant. Lignin has a complex three dimensional structure consists of alkyl phenols (Rangabhashiyam *et al.*, 2013). Lignin is covalently bound with xylans in hardwoods and covalently bound with galactoglucomannans in softwoods (Rangabhashiyam *et al.*, 2013). As a result of huge quantities of wastes being rejected, agricultural waste productions are available in large quantities throughout the world (Rangabhashiyam *et al.*, 2013).

### **2.9.2 Studies of natural form of agricultural waste adsorbents**

There are numerous amount of studies proved on the successful dye adsorption using raw adsorbents prepared from agricultural wastes and used plant parts (Rangabhashiyam *et al.*, 2013). In order to avoid the usage of chemicals, expenditure and its complicated steps of modification, several agricultural wastes were tried in its natural form since they are readily available and economical for dye removal (Rangabhashiyam *et al.*, 2013).

Indian Jujuba Seeds (IJS) (*Zizyphus maruritiana*) is successfully subjected for the removal of dye (Congo red) from aqueous solution (Somasekhara *et al.*, 2012). The dried seed of Indian Jujuba Seeds were crushed and sieved to desired mesh sizes ranging from  $<53\ \mu\text{m}$  to  $<150\ \mu\text{m}$  (Somasekhara *et al.*, 2012). The Langmuir adsorption isotherm present the best fit to the experimental data with a maximum

adsorption capacity of 55.56 mg g<sup>-1</sup> (Somasekhara *et al.*, 2012). The adsorption kinetics follows pseudo-second order kinetics (Somasekhara *et al.*, 2012).

Whole Canola stalks were used as an adsorbent for Acid Orange 7 and Remazol Black 5 dyes from aqueous solution (Hamzeh *et al.*, 2012). It is capable of removing > 90% of dyes with minimal contact times (less than 20 minutes) (Hamzeh *et al.*, 2012). Both Acid Orange 7 and Remazol Black 5 dyes best fits Langmuir isotherm model and the adsorptions kinetics obeys the pseudo second order model (Hamzeh *et al.*, 2012).

Khatod (2013) studied the removal of Methylene Blue using raw orange peel powder. The experimental data fits well in first order kinetic model. Equilibrium was obtained at 18 min with an initial concentration of 2.5 x 10<sup>-5</sup> mg/L dye (Boumediene *et al.*, 2014). Due to the agglomeration of biosorbent, the dye adsorption process decreased with increasing dye concentration resulted by less surface area involved in adsorption process (Khatod, 2013). It was also studied by Boumediene *et al.* (2014) on the ability of orange peel to remove Methylene blue. Batch experiments were conducted with biomass of 1 g, 1 L of known dye solution, 400 rpm agitation rate under 25 ± 1°C to determine kinetic, isotherms and thermodynamic studies (Boumediene *et al.*, 2014).

The removal of Methylene Blue with adsorption into potato peels was also examined by Öktem *et al.* (2012). The kinetic experiments were done and the equilibrium achieved after 60 min with optimal pH of pH 8 (Öktem *et al.*, 2012). Hydroxyl and carboxylic functional groups were found to aid in dye adsorption through FTIR spectra (Öktem *et al.*, 2012). The adsorption of AR37 was also carried out through the use of potato husks. Maximum color removal observed at pH 5.3 and the optimum time and adsorbent dosage were found to be 60 min and 1.0 g/L, respectively (Hilal *et al.*, 2012).

Banana peel powder was employed for the removal of Methylene Blue from spent textile dyeing wastewater. The effect of particle size ( $d < 80 \mu\text{m}$  and  $80 \mu\text{m} < d < 2 \text{ mm}$ ), solution temperature ( $22^\circ\text{C}$  and  $50^\circ\text{C}$ ) and biosorbent's mass were determined (Pishgar *et al.*, 2013). Optimum adsorption was found for  $d < 80 \mu\text{m}$  using 0.1 g mass of adsorbent (Pishgar *et al.*, 2013). Temperature was found to have no significant effect on the amount of dye uptake (Moubarak *et al.*, 2014). Banana peels were also being utilized for the removal of BB159 dye (Pishgar *et al.*, 2013). Batch experiments were applied as a function of pH (3-10), mass of adsorbent (0.2 – 0.8 g), contact time (5 – 120 min), initial dye concentration (50 – 400 mg/L) and agitation speed (100 – 400 rpm) (Pishgar *et al.*, 2013). The total removal of BB159 was achieved at the optimal conditions of pH 9 using 0.4 g of adsorbent when the equilibrium was reached after 60 min (Pishgar *et al.*, 2013).

A new biosorbent almond shell (*Prunus dulcis*) has been investigated in a batch biosorption technique for the removal of Rhodamine 6G (Sentruk *et al.*, 2010). The biosorption kinetics follows pseudo second order model for all the investigated initial concentration of Rhodamine 6G (Sentruk *et al.*, 2010). Equilibrium data fits well with both Langmuir and Freundlich isotherm models. By looking at the best fit of Langmuir isotherm model, it showed a monolayer biosorption capability of almond shell to be as  $32.6 \text{ mg g}^{-1}$  (Sentruk *et al.*, 2010).

The assessment of the Methylene Blue dye adsorption by lotus leaf showed equilibrium data perfectly illustrated by Koble-Corrigan isotherm (Han *et al.*, 2011). The maximum equilibrium capacities of lotus leaf found to be as  $2217 \text{ mg g}^{-1}$  at 293 K (Han *et al.*, 2011). The mechanism follows a pseudo second order mode and might be a chemisorption process. A large number of carbonyl and hydroxyl groups was found to

distribute on the surface of the material according to the result of Fourier transform infrared spectroscopy analysis (Han *et al.*, 2011).

Coconut coir dust were used for the removal of Methylene Blue from aqueous solutions in a batch system (Etim *et al.*, 2012). The adsorption process varied non-linearly with pH but varied linearly with the amount of adsorbent and concentration with time (Etim *et al.*, 2012). Langmuir, Freundlich and Temkin models were found to fit well in the adsorption process with correlation,  $R^2 \geq 0.90$  (Etim *et al.*, 2012). The adsorption kinetics well described by pseudo second order kinetic model. Temperature effect proves that the adsorption was endothermic with a mean change in enthalpy and spontaneous in nature with a mean free energy change (Etim *et al.*, 2012). The results of Fourier transform infrared spectroscopy analysis showed that dye adsorption happened by the means of chemical interaction of the functional groups on the adsorbent surface (Etim *et al.*, 2012).

Pomelo peels was utilized in the removal of RB114 dye (Argun *et al.*, 2014). The experiments were carried out in a pH range in between 2 – 11 (Argun *et al.*, 2014). According to the result shown, the zeta potential values increased with increasing pH of the solution (approximately from –3 mV to –30 mV) (Argun *et al.*, 2014). The repulsive forces resulted from negatively charged dye molecule onto negatively charged surface caused the adsorption process to be retarded (Argun *et al.*, 2014). Kinetic studies indicated that equilibrium was reached in about 90 min (Argun *et al.*, 2014).

## CHAPTER 3

### MATERIALS AND METHODS

#### 3.1 Characteristics of Textile Effluent

For the purpose of this study, textile wastewater sample was collected from a selected textile industry. Textile wastewater was collected during wash out process for excess methylene blue dye on fabric. Wastewater was analyzed according to Standard Method for wastewater. The analysis conducted includes Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Total Dissolved Solids (TDS), Total Suspended Solids (TSS), pH, total solid and turbidity.

##### 3.1.1 Biological Oxygen Demand (BOD)

###### 3.1.1.1 Reagents and Standards

Phosphate buffer: 8.5 g  $\text{KH}_2\text{PO}_4$ , 21.75 g  $\text{K}_2\text{HPO}_4$ , 33.5 g  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$  and 1.7g  $\text{NH}_3\text{C}$  were dissolved in distilled water and diluted to 1L. The pH is 7.2 without further adjustment.

Magnesium sulphate : 22.5g  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  was dissolved in distilled water and diluted to 1L.

Calcium chloride : 27.5g anhydrous  $\text{CaCl}_2$  was dissolved in distilled water and diluted to 1L.

Ferric chloride : 0.25g  $\text{FeCl}_3 \cdot 7\text{H}_2\text{O}$  was dissolves in distilled water and diluted to 1L.

### **3.1.1.2 Preparation of Solution**

One mL each of phosphate buffer, magnesium sulphate, calcium chloride and ferric chloride solutions were added into 1 L of distilled water and was mixed well.

### **3.1.1.3 Sample Preparation**

The effluent was diluted 100x with the prepared BOD dilution water. Textile effluent was neutralized to pH 7. BOD bottles were filled and  $DO_0$  was determined by using DO meter (YSI Pro Plus multi-probe meter). BOD bottles were filled to the rim and trapped gas bubbles were avoided. The BOD bottles were incubated at 20°C for 5 days in BOD incubator.  $DO_5$  were determined after 5 days. Following equation was used to determine the BOD value:

$$BOD_5 = DO_0 - DO_5 \times \text{dilution factor} \quad (\text{Equation 3.1})$$

### **3.1.2 Chemical Oxygen Demand (COD)**

HI 839800 COD reactor and HI 83099 COD meter were used for COD test. The reactor was preheated to 150°C. The supplied syringe was used and 0.2 mL of textile sample was added into the vial. The cap of the vial was replaced tightly and mixed by inverting the vial. Another reagent vial was added with deionized water as control. The vials were inserted into the reactor and heated for 2 hours at 150°C. The vials were allowed to cool to room temperature. The value of COD was determined by using HI 83099 COD meter.

### **3.1.3 Total Dissolved Solids (TDS)**

TDS was determined by using YSI Pro Plus multi-probe meter.

### **3.1.4 Total Suspended Solids (TSS)**

TSS was determined by using Hach DR 5000 UV-Vis spectrophotometer.



### **3.1.5 pH**

pH is measured by using Hanna GLP pH meter HI 111. Varied pH of the effluent samples were adjusted using 0.1 M of NaOH and 0.1 M of HCL.

### **3.1.6 Total Solid**

The mass of an empty porcelain dish was determined. 1mL of textile effluent was filled into the porcelain dish. The content was evaporated at 80°C for 48 hours in an oven. The porcelain dish was weighed after it cooled to room temperature in a desiccator.

Total Solid = Porcelain dish with 1 mL textile effluent – porcelain dish with

$$1 \text{ mL textile effluent after evaporation} \quad (\text{Equation 3.2})$$

### **3.1.7 Turbidity**

Turbidity was determined by using Hach DR 5000 UV-Vis spectrophotometer.

## **3.2 Preparation of Adsorbent**

Kenaf (FH 990) was collected from National Kenaf and Tobacco Board, Selangor while sugarcane bagasse and banana stem was collected from a sugarcane and banana plantation. The supplied adsorbent samples was washed with distilled water and dried in an oven at 40°C for 48 hours to a constant weight. Then, it was grounded into powder and sieved through 1 mm siever.

## **3.3 Characteristics of Adsorbents**

The surface area of the adsorbents were analyzed by using BET surface area analyzer and the surface morphology of three adsorbents was visualized by a scanning electronic microscope. FTIR spectroscopy (Perkin Elmer Frontier FT-IR/FIR Spectrometers) was used to identify the presence of certain functional groups in the adsorbent. Infra spectra

of the adsorbents were obtained by accumulating 8 scans at spectral resolution of  $1\text{cm}^{-1}$  from  $4000\text{ cm}^{-1}$  to  $600\text{ cm}^{-1}$ .

### **3.4 Adsorption Studies**

Adsorption studies were carried by using synthetic methylene blue to determine the maximum parameters for adsorption treatment. Different absorbance was identified by calibrating synthetic methylene blue at 10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L, 50 mg/L, 60 mg/L and 70 mg/L.

#### **3.4.1 Effect of pH**

50 mL of textile effluent was poured into conical flasks. Varied pH of the effluent samples (pH 2, pH 4, pH 6, pH 8 and pH 10) were adjusted using 0.1 M of NaOH and 0.1 M of HCL in different conical flasks. 0.5 g of adsorbents was added and the conical flasks were shaken in a water bath shaker under 150 rpm for 300 min. Temperature ( $60^{\circ}\text{C}$ ) and concentration (70 mg/L) of the adsorbents was maintained. After reaching the equilibrium, the mixtures was filtered using syringe filter. Three replicates of dyes that had been filtrated were analyzed by using Shidmadzu UV-1800 spectrophotometer after centrifuged.

#### **3.4.2 Determination of Optimum Agitation Time**

50 mL of textile effluent was poured into conical flasks. 0.5 g of adsorbents was added into the conical flasks. Conical flasks was put into the water bath shaker (Daihan Wisebath WSB-30) for various time period ranging from 5 min to 300 min under 150 rpm. Temperature ( $60^{\circ}\text{C}$ ), initial concentration (70 mg/L) and pH (pH 8) of the adsorbent was maintained. After reaching the equilibrium, the mixtures was filtered

using syringe filter. Three replicates of dyes that had been filtrated were analyzed by using Shidmadzu UV-1800 spectrophotometer after centrifuged.

### **3.4.3 Effect of Initial Concentration**

50 mL of textile effluent was poured into conical flasks. 0.5 g of adsorbents was added into the conical flasks. Varied concentration of adsorbate (50 mg/L, 100 mg/L, 150 mg/L and 200 mg/L) was added and the conical flasks were shaken under optimum agitation time. Temperature (60°C) and pH (pH 8) of the adsorbents was maintained. After reaching the equilibrium, the mixtures was filtered using syringe filter. Three replicates of dyes that had been filtrated were analyzed by using Shidmadzu UV-1800 spectrophotometer after centrifuged.

### **3.4.4 Effect of Temperature**

50 mL of textile effluent was poured into conical flasks. 1g of adsorbents was added into the conical flasks. Various temperature was used to determine the effect of temperature on adsorbents such as 20°C, 40°C, 60°C and 80°C. Initial concentration (70 mg/L) and pH (pH 8) were adjusted and the mixtures were shaken under 60°C at optimum agitation time. After reaching the equilibrium, the mixtures was filtered using syringe filter. Three replicates of dyes that had been filtrated were analyzed by using Shidmadzu UV-1800 spectrophotometer after centrifuged.

## **3.5 Isotherms**

### **3.5.1 Removal Efficiency of Adsorbents**

The following formula that was used to determine the decolouration efficiency of each experiments in percentage by calculating the difference concentration of the dye before and after the treatment (Torres *et al.*, 2009).

$$\% \text{ Dye Removal} = \frac{Ab_1 - Ab_2}{Ab_2} \times 100 \quad (\text{Equation 3.3})$$

Where,

$Ab_1$  = Initial concentration of dye

$Ab_2$  = Concentration of dye after treatment

### 3.5.2 Adsorption Capacity

This equation was used to calculate the adsorption capacity of the adsorbents by involving the weight and volume of the adsorbents (Deng *et al.*, 2011).

$$q_s = \frac{(C_0 - C_s)}{M} \times V \quad (\text{Equation 3.4})$$

Where,

$q_s$  (mg g<sup>-1</sup>) = Adsorption capacity

$V$  (L) = Volume

$M$  (g) = Weight of the adsorbent

$C_0$  (mg L<sup>-1</sup>) = Initial Concentration of adsorbate

$C_s$  (mg L<sup>-1</sup>) = Equilibrium concentration of substrates in the solution

### 3.5.3 Langmuir Isotherm

The Langmuir isotherm assumes that adsorption occurs on a homogeneous monolayer surface containing sites with uniform energy with a finite number of identical sites. It also assumes there is no interaction between the adsorbed molecules (Xing *et al.*, 2010).

$$\frac{1}{q_s} = \frac{1}{bQ_m} + \frac{C_s}{Q_m} \quad (\text{Equation 3.5})$$

Where,

$q_s$  (mg g<sup>-1</sup>) = Adsorption capacity

$Q_m$  (mg g<sup>-1</sup>) = Maximum amount of adsorption

$b$  (L mg<sup>-1</sup>) = Adsorption equilibrium constant

$C_s$  (mg L<sup>-1</sup>) = Equilibrium concentration of substrates in the solution

#### 3.5.4 Freundlich Isotherm

The Freundlich expression is for a multilayer sorption to occur and it is an empirical equation for adsorption on heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface (Xing *et al.*, 2010).

$$\log q_s = \log K_F + \frac{1}{n} \log C_s \quad (\text{Equation 3.6})$$

Where,

$q_s$  (mg g<sup>-1</sup>) = Adsorption capacity

$K_F$  ((mg/L)(L/mg)<sup>1/n</sup>) = Freundlich constant related to adsorption  
capacity of adsorbent

$n$  = Freundlich exponent related to adsorption  
intensity

$C_s$  (mg L<sup>-1</sup>) = Equilibrium concentration of substrates in the  
solution

### 3.6 Adsorption Thermodynamic

Energy and entropy are key elements to be evaluated in any interaction process design. Thermodynamic parameters including Gibbs free energy change ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) were calculated using the following equations to evaluate the feasibility and endothermic nature of the adsorption process (Zhang et al., 2011).

$$\Delta G^\circ = -RT \ln K_d \quad (\text{Equation 3.7})$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (\text{Equation 3.8})$$

Where,

$R$  ( $\text{J K}^{-1} \text{mol}^{-1}$ ) = Gas constant ( $8.3145 \text{ J K}^{-1} \text{mol}^{-1}$ )

$T$  (K) = Temperature

$K_d$  ( $\text{m}^3 \text{mol}^{-1}$ ) = Equilibrium constant

### 3.7 Determination of Calorific Value by using Bomb Calorimeter (Parr 1341 Plain Jacket Calorimeter)

Adsorbates were weighted (1 g). The bomb was set on an A38A support stand and a 10 cm length of Parr 45C10 nickel alloy wire was fasten between the two electrodes. Fuel capsule with its weighed adsorbate was placed in the electrode loop and the wire was bend downward towards the surface of the charge. 1 mL of distilled water was placed at the bottom of the bomb as a sequestering agent. The bomb head with adsorbate was then moved from support stand to the bomb cylinder. The bomb was next filled with oxygen to 30 atm and placed into the calorimeter bucket filled with 2000 mL of distilled water. Two ignition lead wires were pushed into the terminal sockets on the bomb head while the stirrer was left to run for 5 minutes to reach equilibrium before a measured run. Calorimeter was fired after 5 minutes by pressing the ignition button. Temperatures

were recorded at one-minute intervals until the temperature reached a maximum and dropped very slowly. The motor was stopped and the bomb was lifted out of the bucket by removing the ignition leads. The gas pressure was released from the bomb and the head was lifted out of the cylinder. Interior surfaces was washed with a jet of distilled water. Unburned pieces of fuse wire was then measured. Finally, bomb washing was titrated using standard sodium carbonate solution using methyl red indicator.

### 3.7.1 Calculation for Temperature Rise

$$t = t_c - t_a - r_1(b - a) - r_2(c - b) \quad (\text{Equation 3.9})$$

Where,

$t_a$  = Temperature at time of firing

$t_c$  = Temperature at equilibrium

$r_1$  = Rate at which the temperature was rising during the 5 minute period  
before firing

$r_2$  = Rate at which the temperature was rising during the 5 minute period  
after time of equilibrium

$a$  = Time of firing

$b$  = Time when the temperature reaches 60% of the total rise

$c$  = Time at the beginning in which the rate of temperature changes has  
become constant

### 3.5.2 Calculation for Gross Heat of Combustion

$$H_g = \frac{tW - e_1 - e_2 - e_3}{m} \quad (\text{Equation 3.10})$$

Where,

$t$  = Temperature rise

$W$  = Standardization of benzoic acid

$e_1$  = Correction in calories for heat of formulation of nitric acid

$e_2$  = Correction of calories for heat of formulation of sulphuric acid

$e_3$  = Correction in calories for heat of combustion of fuse wire

(2.3)(cm)



## CHAPTER 4

### RESULTS AND DISCUSSION

#### 4.1 Characteristics of Textile Effluent

##### 4.1.1 Characteristics of Textile Effluent before the Treatment

Pt-Co method is a common comparison method used to compare the intensity of yellow-tinted samples in order to evaluate pollution levels in wastewater. Since this research only targeted on methylene blue, hence, this method is not suitable to be used in this research. Table 4.1 showed the characteristics of textile effluent as compared to wastewater discharged effluent of Standard A and Standard B. pH of wastewater effluent was alkaline which displayed pH 11.12. This might due to the present of methylene blue dye in the wastewater which caused the wastewater to be alkaline.

Table 4.1: Characteristics of textile effluent.

	Effluent	Standard A	Standard B
pH	11.12	6.0-9.0	5.5-9.0
Total Solid	1.05 g	-	-
Total Suspended Solid	1.05 mg/L	50 mg/L	100 mg/L
Turbidity	354 FAU	-	-
TDS	96.9 ppm	-	-
BOD	206 mg/L	20 mg/L	50 mg/L
COD	25500 mg/L	80 mg/L	250 mg/L

Total solid and total suspended solid of the wastewater effluent were 1.05 g and 1.05 mg/L, respectively. Low value in both total solid and total suspended solids indicated that the amount of solid and suspended particles in the wastewater effluent are lower than the standard allowed. The turbidity of wastewater effluent was 354 FAU. Turbidity

is a good parameter to measure the status of polluted water because higher concentration of dyes, ions and other polluting agents will caused the wastewater becomes turbid and polluted.

The amount of total dissolved solids in wastewater effluent was 96.9 ppm. Total dissolved solids display the pollution strength of the wastewater. Higher concentration of total dissolved solids will convey odors of wastewater effluent. BOD<sub>5</sub> and COD of wastewater effluent sample were 206 mg/L and 25500 mg/L, respectively. By comparing with Standard A and Standard B, value of both BOD<sub>5</sub> and COD were extremely high. High reading of BOD<sub>5</sub> and COD indicated that the amount of organic matter in wastewater effluent is high.

#### **4.1.2 Characteristics of Effluent after the Treatment**

Table 4.2 showed the characteristics of textile effluent before and after the treatment process for dye removal using kenaf, banana stem and sugarcane. Based on the results, water quality of the effluent improved after the treatment process. The textile wastewater was highly alkaline (pH = 11.12) before the treatment due to the presence of sodium hydroxide and silica during dyeing process. pH of the textile effluent decreased to neutral pH after the dye removal process which display a pH value of 7.68, 7.70 and 7.65 for kenaf, banana stem and sugarcane bagasse, respectively. Methylene blue is a basic dye, hence, the reduction of methylene blue present in effluent will reduce the pH value.

Table 4.2: Characteristics of textile effluent before and after treatment.

Analyst	Initial	After Treatment			Reduction (%)		
		Kenaf	Banana Stem	Sugarcane Bagasse	Kenaf	Banana Stem	Sugarcane Bagasse
pH	11.12	7.68	7.70	7.65	30.94	30.76	31.21
Total Solid (g)	1.05	1.03	1.01	1.03	1.90	3.81	1.90
Total Suspended Solid (mg/L)	1.05	0.09	0.08	0.09	91.43	92.38	91.43
Turbidity (FAU)	354	22	19	21	93.79	94.63	94.07
TDS (ppm)	96.90	96.20	95.76	96.30	0.72	11.76	0.62
BOD <sub>5</sub> (mg/L)	206	163	142	171	20.87	31.07	16.99
COD (mg/L)	25500	10640	10312	10937	58.27	59.56	57.11
Percentage of Dye Removal (%)	-	96.96	97.82	97.42	-	-	-

Besides, total solid and total dissolved solid (TDS) also showed slight improvement after adsorption treatment of less than 12 %. There is no significant change as compared to the initial values. This probably due to the fact that after the dyeing process, most of the solid such as wax will be filtered and removed before the wastewater is discharged into water bodies. Thus, the remaining total solid and total dissolved solid in the wastewater were very minimum.

Total suspended solids and turbidity were two parameters that showed significant improvement with the applied adsorption treatment. These two parameters showed percentage differences of more than 90 %. The amount of suspended solids was reduced from initial value of 1.05 mg/L to 0.09 mg/L, 0.08 mg/L and 0.09 mg/L by kenaf, banana stem and sugarcane bagasse, respectively. This contributes to a decrease in turbidity of wastewater effluent from 354 FAU to 22 FAU, 19 FAU and 21 FAU in treatment with kenaf, banana stem and sugarcane bagasse, respectively. Removal of dye after adsorption treatment caused the total suspended solids and turbidity of the wastewater to decrease. Mahmoud (2010) stated that there is a relationship between amount of suspended solids and turbidity. Turbidity is the measure of water clarity influenced by the amount of suspended solid in the water body. Thus, dyes and pigments, binder, solvents and other inorganic substances may produce turbidity in the water which caused by different types of suspended materials such as colloidal and sub colloidal (Mahmoud, 2010).

BOD<sub>5</sub> and COD are the two important parameters to indicate the degree of pollution in the textile effluent. From Table 4.3, BOD<sub>5</sub> values for the wastewater effluent was reduced from 206 mg/L to 163 mg/L, 142 mg/L and 171 mg/L by kenaf, banana stem and sugarcane bagasse, respectively. The higher BOD<sub>5</sub> value at the initial stage was

mainly contributed to the presence of organic matter since dye consists of a lot of organic compounds. These organic materials will then decomposed by bacteria and caused high BOD<sub>5</sub> level. High BOD<sub>5</sub> reading indicates low dissolved oxygen (DO) level in water body which is unfavorable for aquatic ecosystem. Hence, a decline in BOD<sub>5</sub> value of the wastewater via adsorption process is necessary to improve the wastewater quality. BOD<sub>5</sub> value can be reduced through the removal of excess organic compounds such as dyes and pigments from the wastewater.

COD is used to measure the amount of organic pollutants present in water body. The textile effluent after treatment showed lower COD value which were 10640 mg/L, 10312 mg/L and 10937 mg/L for kenaf, banana stem and sugarcane bagasse, respectively, as compared to the raw wastewater effluent which was 25500 mg/L. COD value reduced after adsorption treatment as dyes (organic compounds) had been removed from wastewater. Low concentration of organic compounds will give low COD value. BOD<sub>5</sub> and COD value could be further reduced by incorporate with other wastewater processes within a wastewater treatment plant.

Table 4.3 showed the percentage of pollutant reduction for all the analysts. Total dissolved solids (TDS) was the least reduced after adsorption treatment which is in between 0.62 % - 11.76 %, followed by total solid and BOD<sub>5</sub> with reduction at 1.90 % - 3.81% and 16.99 % - 31.07 %, respectively. pH and COD was better reduced at 30.76 % - 31.21 % and 57.11 % - 59.56 %, respectively. Two parameters that showed significant improvements at 91.43 % - 92.38 % and 93.79 % - 94.63 %, were total suspended solid and turbidity, respectively.

Table 4.3: Percentage reduction of pollutant in textile effluent.

Analyst	Minimum (%)	Maximum (%)	Mean (%)
pH	30.76	31.21	30.99
Total Solid (g)	1.90	3.81	2.86
Total Suspended Solid (mg/L)	91.43	92.38	91.91
Turbidity (FAU)	93.79	94.63	94.21
TDS (ppm)	0.62	11.76	6.19
BOD <sub>5</sub> (mg/L)	16.99	31.07	24.03
COD (mg/L)	57.11	59.56	58.34
Percentage of Dye Removal (%)	96.96	97.82	97.39

Based on Table 4.2 and Table 4.3, all agro-wastes were able to remove more than 95 % of methylene blue dye from wastewater. Percentage of methylene blue dye removal were 96.96 %, 97.82 % and 97.42 % for kenaf, banana stem and sugarcane bagasse treatments, respectively. The sequence of dye removal ability according to percentage of dye removal was banana stem > sugarcane bagasse > kenaf.

## 4.2 Characteristics of Adsorbent

Characterization of kenaf, banana stem and sugarcane bagasse were carried out by using FTIR (Fourier transform infrared spectroscopy) analysis, field emission scanning electron microscopy (FESEM) and surface area and pore size analysis (BET analysis). It is crucial to determine the characteristic of adsorbents as their physical and chemical properties can influence the adsorption behavior.

#### 4.2.1 FTIR (Fourier transform infrared spectroscopy) Analysis

FTIR spectra was employed to ascertain the bond types, structures and functional groups in three agro-wastes and to determine the groups responsible for the adsorption of the dye. Figure 4.1 showed the FTIR spectra of kenaf, banana stem and sugarcane bagasse. Kenaf showed broadband at  $3338.47\text{ cm}^{-1}$  which typically attributed to hydroxyl group (O-H group). The adsorption band at  $1028.40\text{ cm}^{-1}$  and  $1240.80\text{ cm}^{-1}$  are attributed with C-O groups. Besides, the other adsorption at  $1421.23\text{ cm}^{-1}$  and  $1596.07\text{ cm}^{-1}$  are attributed to aromatic compounds with C=C bond.

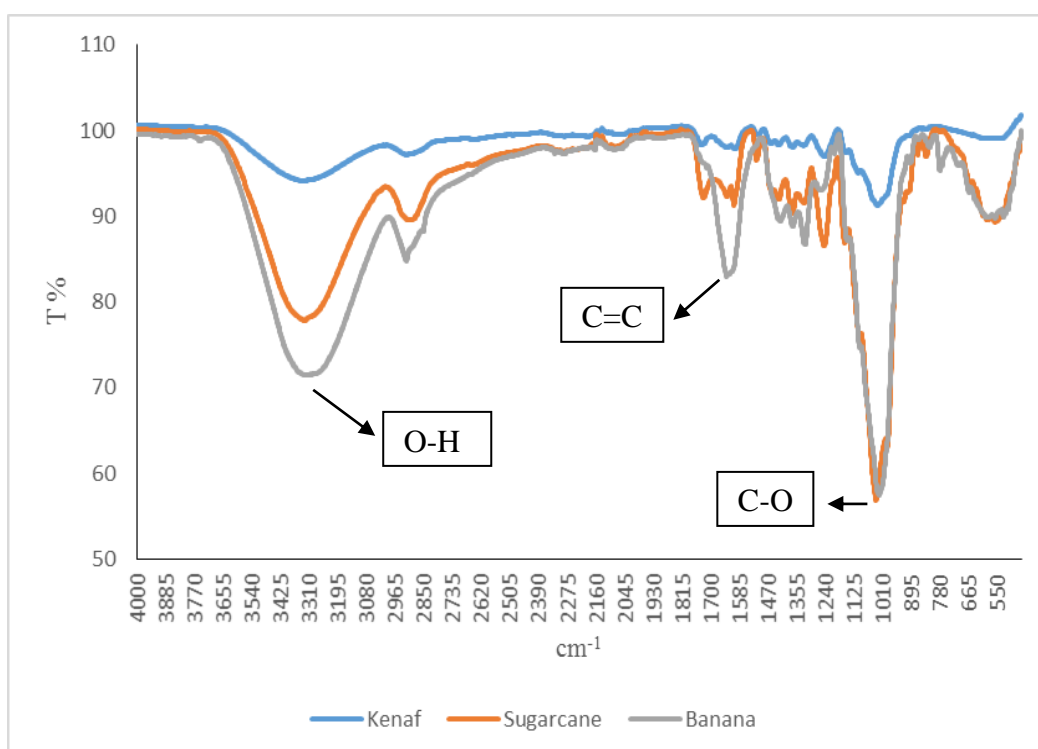


Figure 4.1: FTIR spectra of kenaf, banana stem and sugarcane bagasse.

In the case for banana stem, the common and large band located at  $3328.01\text{ cm}^{-1}$  can be attributed to O-H group. On the other hand, the adsorption band at  $1028.61\text{ cm}^{-1}$  and  $1243.80\text{ cm}^{-1}$  can be assigned to C-O groups while  $1513.54\text{ cm}^{-1}$  and  $1631.64\text{ cm}^{-1}$  were attributed to C=C bond in aromatic compounds.

Sugarcane bagasse showed an intense band at  $3335.33\text{ cm}^{-1}$  attributed to O-H group. The region of spectrum at  $1033.67\text{ cm}^{-1}$ ,  $1102.25\text{ cm}^{-1}$  and  $1157.45\text{ cm}^{-1}$  are attributed to ethers groups (C-O groups). Meanwhile, an adsorption band at  $1425.65\text{ cm}^{-1}$  could be attributed to C=C bond as in aromatic compounds.

The function of infrared (IR) spectroscopy is to judge the adsorption of IR radiation by materials as the atoms vibrate about their bonds (Kelesoğlu, 2007). According to Aseel *et al.* (2014), the existence of hydroxyl groups, ethers groups and aromatic compounds proved to help in physical adsorption. Hence, it can be concluded that all agro-wastes adsorbents would be able to perform high adsorption properties due to the presence of hydroxyl groups, ethers groups and aromatic compounds.

#### **4.2.2 Morphology Observation via FESEM (Field Emission Scanning**

##### **Electron Microscopy)**

Morphology observation via field emission scanning electron microscopy of kenaf, banana stem and sugarcane bagasse were shown in Plate 4.1, Plate 4.2 and Plate 4.3, respectively. As shown in Plate 4.1, kenaf displayed a rigid and highly ordered fibrils. The result of this study is in agreement with the findings of Yousif *et al.* (2012) that reported the morphology of untreated kenaf (Yousif *et al.*, 2012).



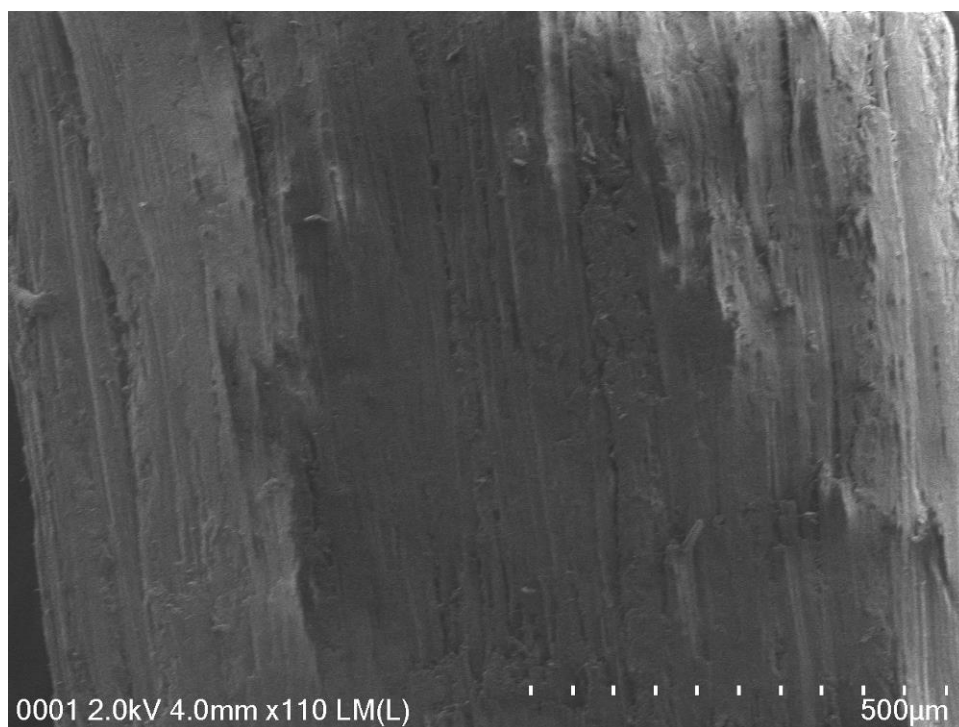


Plate 4.1: Field emission scanning electron microscopy for kenaf.

Plate 4.2 and Plate 4.3 display the FESEM images of banana stem and sugarcane bagasse, respectively. Both banana stem and sugarcane bagasse have rough and irregular surfaces. However, banana stem is apparently rougher than sugarcane bagasse with some micropores on the surface. Based on the research done by Baek *et al.* (2010), rough and porous surface offer better adsorption process. Hence, based on the morphology of all the adsorbents, banana stem would have the most favourable morphological conditions for adsorption.

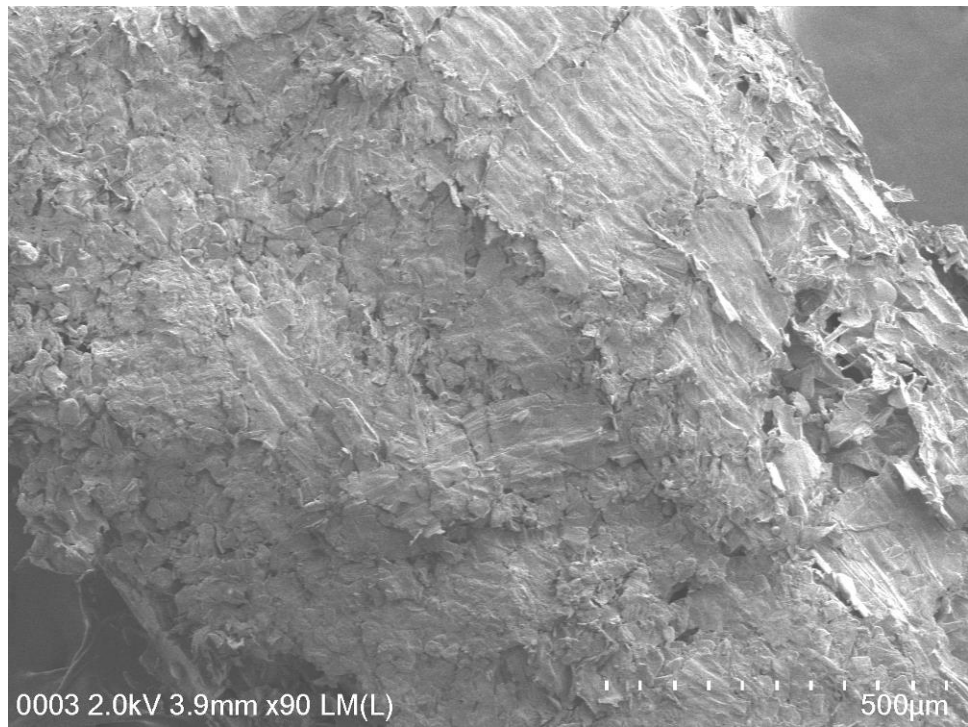


Plate 4.2: Field emission scanning electron microscopy for banana stem.

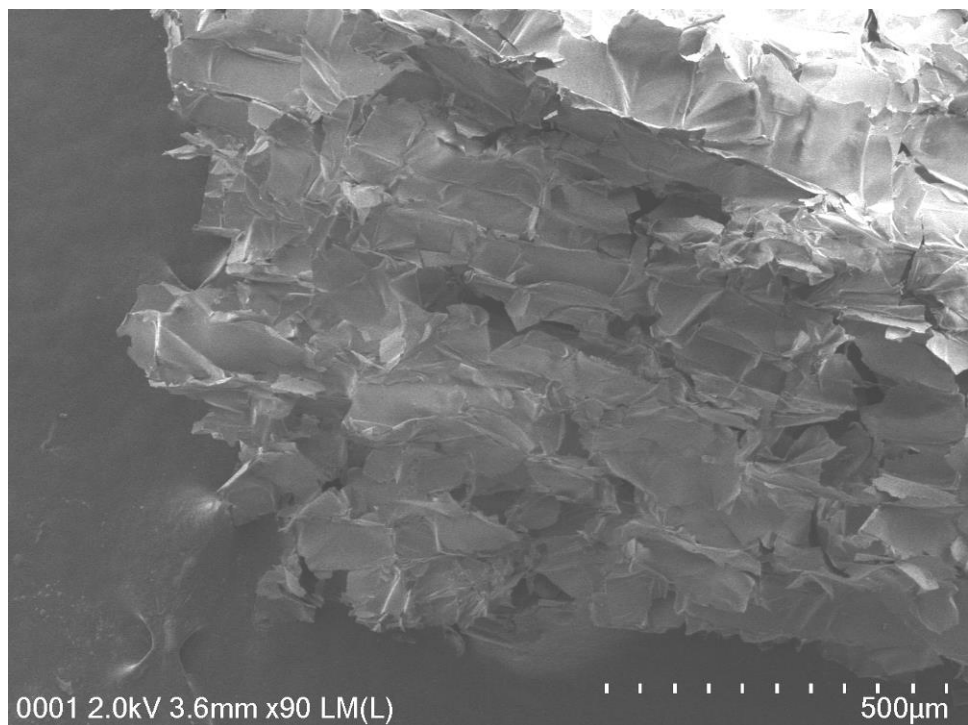


Plate 4.3: Field emission scanning electron microscopy for sugarcane bagasse.

### 4.2.3 BET Surface Area Analysis of Agro-wastes

The specific surface area of kenaf, banana stem and sugarcane bagasse were determined by BET method from adsorption – desorption isotherm of nitrogen. Table 4.4 showed the result of BET surface area, pore volume and average pore size analysis of kenaf, banana stem and sugarcane bagasse. The values of BET surface area, pore volume and pore size of kenaf was 1.2630 m<sup>2</sup>/g, 0.0029 cm<sup>3</sup> and 91.6521 Å, respectively while the value for banana stem was 0.9613 m<sup>2</sup>/g, 0.0032 cm<sup>3</sup>/g and 132.0609 Å, respectively. Comparatively for sugarcane bagasse, the corresponding values are 0.3438 m<sup>2</sup>/g, 0.0007 cm<sup>3</sup>/g and 79.6355 Å, respectively.

In line with the results showed in Table 4.4, kenaf, banana stem and sugarcane bagasse showed micropore characteristics. Kenaf showed highest surface area followed by banana stem and lastly sugarcane bagasse. Kenaf exhibits surface area of 1.2620 m<sup>2</sup>/g followed by banana stem and sugarcane bagasse which are 0.9613 m<sup>2</sup>/g and 0.3438 m<sup>2</sup>/g, respectively.

Moreover, by comparing the pore size of all the agro-waste adsorbents, banana stem showed the largest pore size (132.0609 Å) followed by kenaf (91.6521 Å) and sugarcane bagasse (Å). Hence, larger pore size are able to enhance the adsorption process for dye removal.

Table: 4.4: BET surface area characterization.

	Surface area (m <sup>2</sup> /g)	Pore Volume (cm <sup>3</sup> /g)	Pore size (Å)	
<b>Kenaf</b>	1.2630	0.0029	91.6521	Micropore
<b>Banana Stem</b>	0.9613	0.0032	132.0609	Micropore
<b>Sugarcane bagasse</b>	0.3438	0.0007	79.6355	Micropore

### 4.3 Adsorption Studies

Various operational parameters were selected to investigate adsorption characteristics of kenaf, banana stem and sugarcane bagasse for methylene blue dye adsorption from aqueous solution. These parameters include pH, agitation time, initial concentration and temperature.

#### 4.3.1 Calibration Curve of Methylene Blue

Different absorbance was identified by calibrating the methylene blue dye at various concentrations namely 10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L, 50 mg/L, 60 mg/L and 70 mg/L. Figure 4.2 showed the graphical representation of the calibration of methylene blue dye. The coefficient values of the calibration curves was 0.9961 for methylene blue dye. The calibrated results were referred to identify respective dye removal capability of adsorbents.

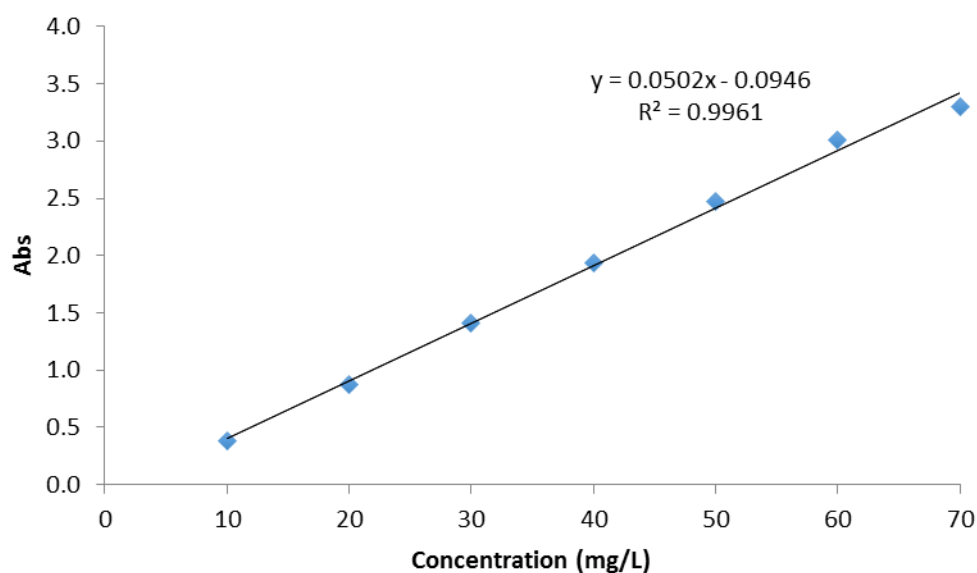


Figure 4.2: Calibration of methylene blue dye using various dye concentrations.

### 4.3.2 Effect of pH

The pH of the aqueous solutions is one of the vital controlling parameter in the adsorption process. Chemical nature of the adsorbate and adsorbent decide the optimal pH value of the absorption process (Viera *et al.*, 2011). Hence, the determination of optimum pH was carried out in an aqueous solution of 70 mg/L concentration with constant temperature (60°C), adsorbent dosage (0.5 g) and a fixed agitation time in methylene blue dye in different range of pH (pH 2 – 10).

In Figure 4.3, the maximum removal of methylene blue dye was noted at pH 8 for the three adsorbents (kenaf, banana stem and sugarcane bagasse) were 95.84 %, 97.69 % and 95.48 %, respectively. pH 2 showed 62.51 % to 82.04 % dye removal percentage in while pH 4 removed 94.09 % to 95.24 % dye for kenaf, banana stem and sugarcane bagasse. On the other hand, pH 6 displayed a range of 94.72 % to 97.42 % of dye removal capability and a range of 94.78 % to 95.57 % dye removal percentage for pH 10. Therefore, optimum pH 8 was selected for further studies.

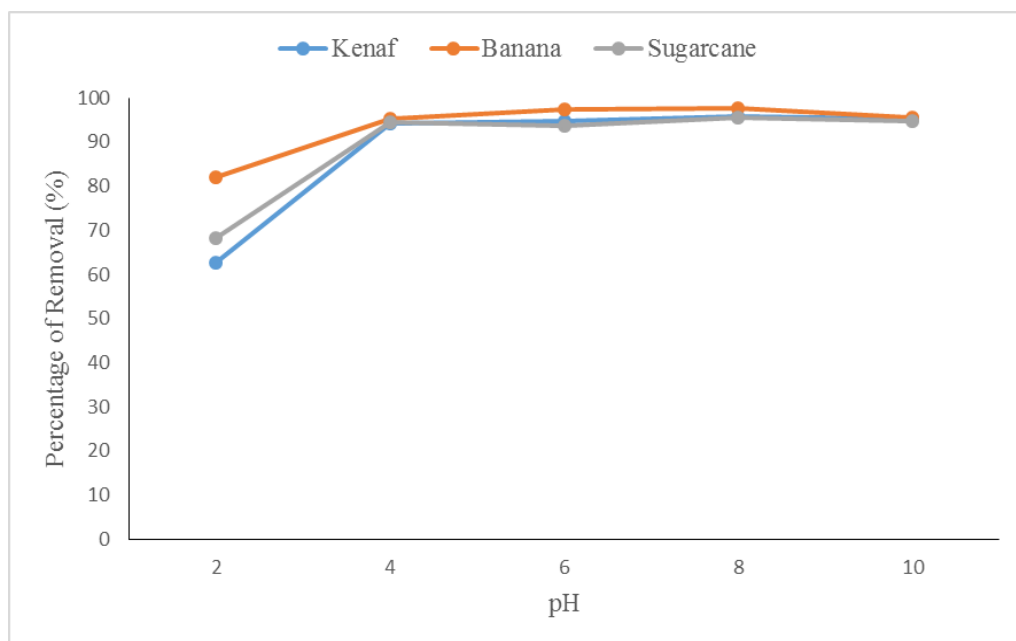


Figure 4.3: Determination of optimum pH of adsorbents for methylene blue dye in 70 mg/L concentration.

The adsorption capacity of the absorbent is affected by pH of the dye solution through modification of the state of ionization of the binding groups either by increasing or decreasing the competition between the protonated species and adsorbate molecules for the active sites (Viera *et al.*, 2011). The pH values were selected by considering the electrostatic attraction that exists between the negatively charged surfaces of absorbent mainly due to cationic dye (Pavan *et al.*, 2008). Preliminary tests were carried out to obtain the most favorable pH. Dye removal percentage under slightly alkaline condition using banana stem found the most effective with the highest removal percentage (97.69 %) of methylene blue dye. This is due to the present of charged species that influence the adsorption process. With dominated negatively charged species responsible for acquiring negative charge on the surface of the sample, the increasing electrostatic attraction between positively charged adsorbate species and negatively charged adsorbent particles would lead to an increased in dye adsorption (Khattri *et al.*, 2009). Similar trends were reported for the adsorption of methylene blue onto Fe(III)/Cr(III) hydroxide (Namasivayam and Sumithra, 2005) and adsorption of methylene blue onto yellow passion fruit peel (Pavan *et al.*, 2008).

#### **4.3.3 Determination of Optimum Agitation Time**

Optimum agitation time were conducted to evaluate the time at which equilibrium was reached for three different agro-wastes adsorbents. The results of optimum agitation time for removing methylene blue dye using kenaf, banana stem and sugarcane bagasse is presented in Figure 4.4. The effect of agitation time (5 – 300 min) on the adsorption capacity of kenaf, banana stem and sugarcane bagasse for methylene blue dye were studied at pH 8, 0.5 g adsorbent dose, 70 mg/L initial dye concentration and at 60 °C.

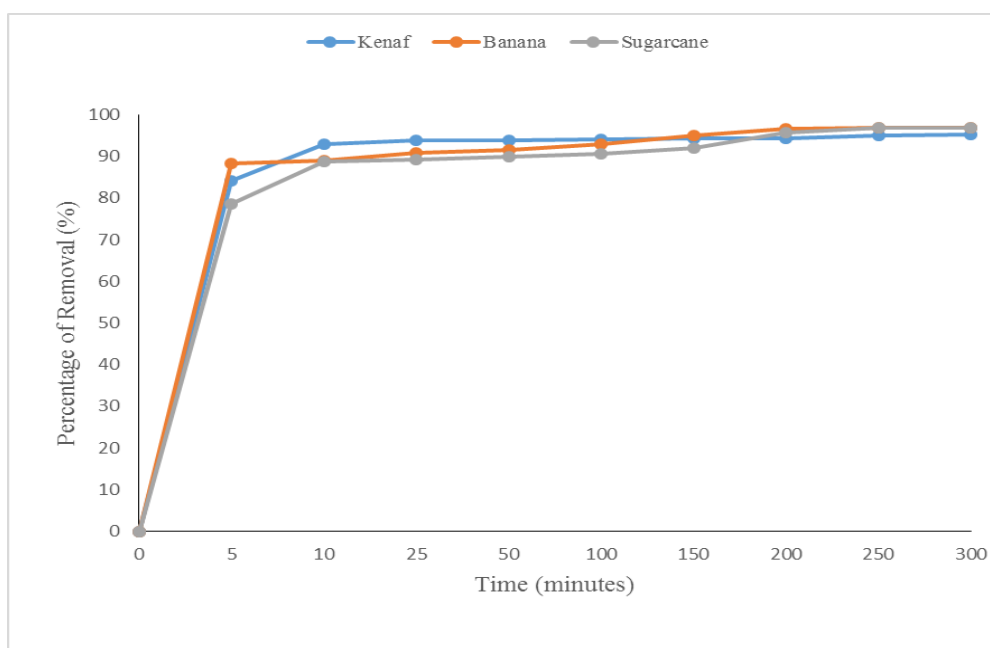


Figure 4.4: Determination of optimum agitation time for removing methylene blue dye.

The results showed a rapid increase of dye removal percentage at the initial stage and then reached the equilibrium. This trend is observed as high number of vacant binding active sites were available for dye at the initial stage and these binding sites were covered slowly that caused a decrease in adsorption rate to finally attain the equilibrium (Noreen *et al.*, 2013). The equilibrium agitation time required for removing methylene blue using kenaf was 25 minutes with 93.81 % of dye removal efficiency. However, banana stem and sugarcane bagasse were slower to reach equilibrium with higher removing efficiency of 96.60 % and 95.62 % at 200 minutes of agitation time. Kenaf was able to reach equilibrium within a shorter time (25 minutes) as compared to banana stem and sugarcane bagasse (200 minutes). This was due to the larger surface area of kenaf as according to BET surface area analysis. Larger surface area enable kenaf to perform rapid adsorption process which result in rapid equilibrium.

The agitation time is one of the influential factors for the development of surface charges at solid solution interface (Tiong, 2013). It was indicated that maximum agitation time plays an important role for removing dyes from aqueous solution by adsorption at a fixed concentration, pH and temperature. The result of present study for methylene blue dye removing ability is in agreement with the findings of Khattri *et al.* (2009) who reported that an establishment of equilibrium in dye adsorption in a short time and a sharp uptake of dyes indicate the efficiency of the adsorbent. The rest of the experiments were conducted using these optimum agitation times for kenaf, banana stem and sugarcane bagasse, respectively, to remove methylene blue dye from aqueous solution.

#### 4.3.4 Effect of Initial Concentration

The adsorption potential of kenaf, banana stem and sugarcane bagasse were determined at several different initial concentrations (10 – 70 mg/L) conducted under equilibrium condition of 60 °C, pH 8, adsorbent dosage of 0.5 g and a fixed agitation time of 25 min (kenaf) and 200 min (banana stem and sugarcane bagasse), respectively. The results were shown in Figure 4.5.

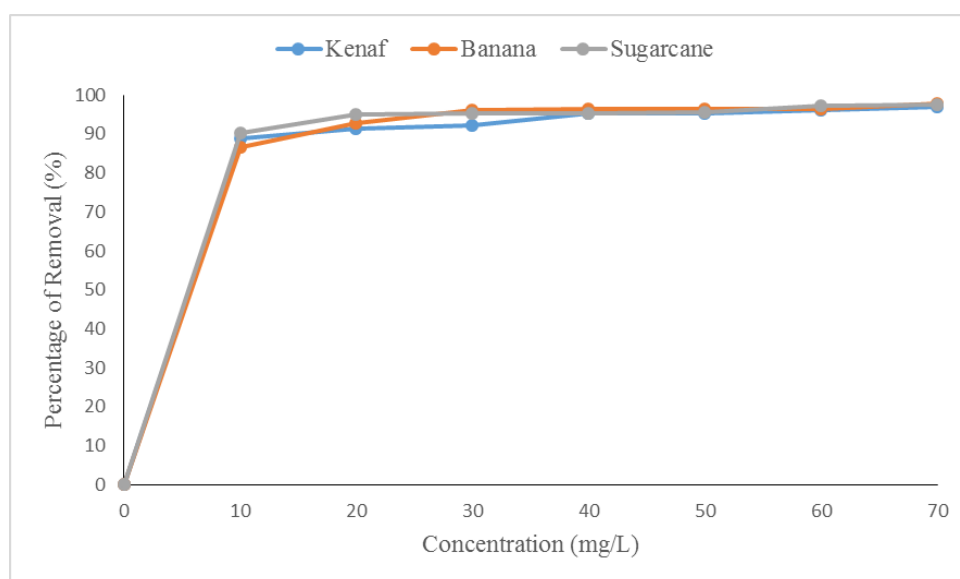


Figure 4.5: Determination of optimum initial concentration for methylene blue dye.



As illustrated in Figure 4.5, dye removal efficiency increases with increasing initial dye concentration to reach an equilibrium state. Kenaf, banana stem and sugarcane bagasse showed highest removal percentage at the concentration of 70 mg/L with 96.96 %, 97.82 % and 97.42 %, respectively. In order to overcome the diffusive mass transfer resistance of all molecules between adsorbents and adsorbate, initial dye concentration is an important driving force (Khataee *et al.*, 2013). Hence, a higher initial concentration gives a crucial driving force to overcome all resistances of dye between aqueous and solid phases thus increased the dye uptake.

Based on Amel *et al.* (2012), an increase in the initial ions concentrations of methylene blue will enhance the number of collisions resulted between the dye ions and the adsorbent, thus, improves the adsorption process. Similar trends was noticed for the adsorption of basic dye onto neem sawdust which concluded that the amount of surface sites available for adsorption will reduced after a lapse of time which will then repulse the solute molecules of solid and bulk phases (Khattri and Singh, 2009).

#### **4.3.5 Effect of Temperature**

Present study considered a series of experiment using different temperature such as 40°C, 60 °C, 80 °C and 100 °C at pH 8, 0.5 g adsorbent dosage, initial dye concentration of 70 mg/L and respective agitation time (25 minutes for kenaf and 200 minutes for banana stem and sugarcane bagasse). The result as illustrated in Figure 4.6 indicated that kenaf, banana stem and sugarcane bagasse showed an optimum dye removal capability of 96.96 %, 97.82 % and 97.42 %, respectively at 60 °C. The order of effective temperature for methylene blue dye removal was 60°C > 40 °C > 80°C > 20 °C > 100 °C for all types of adsorbents.

Temperature has a pronounced effect on the adsorption capacity of the adsorbents. An alteration in chemical potentials might explained the differences occurred in the extent of adsorption with temperature. It is interlinked to the solubility of the adsorbate species that increase with a rise in temperature, while decreases in chemical potential. Both temperature and solubility of adsorbate species work in the same direction. An equilibrium process can be referred to the adsorption reaction at any interface between two phases (Khatttri and Singh, 2009).

Figure 4.6 shows that 60 °C was a better temperature as compared to lower temperature, 40 °C. Jayarajan *et al.* (2011) stated that an elevation in the mobility of the large ion would due to an increase in temperature and produce a swelling effect within the internal structure of the nano-porous material hence, enable further penetration of large size molecules. However, 60 °C showed the highest adsorptive capacity as compared to 80 °C and 100 °C. This may be due to the reason that 80 °C and 100 °C is an extreme temperatures that will alter and destroyed the structure of kenaf, banana stem and sugarcane bagasse and caused a reduction in adsorption capability. High temperature will destroyed the covalent bond, thus, reduce the holding capacity of the adsorbents to trap dye molecules. The adsorption capacity largely rely on the chemical reaction between the functional groups of the adsorbent surface and adsorbate (Jayarajan *et al.*, 2011).

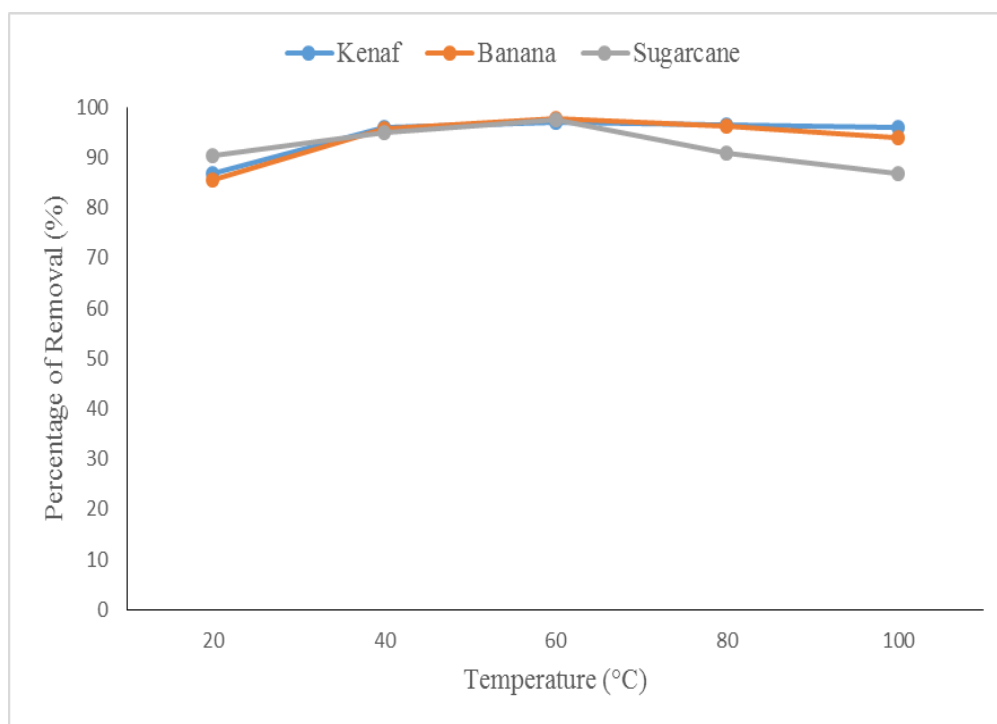


Figure 4.6: Determination of optimum temperature of kenaf, banana stem and sugarcane bagasse for methylene blue dye.

#### 4.3.6 Maximum Adsorption Capacity under Optimum Condition

After conducting a series of adsorption batch mode studies, the optimum condition such as pH, time, initial concentration and temperature were obtained. The optimum pH for kenaf, banana stem and sugarcane bagasse was pH 8 whereas the optimum agitation time for kenaf was 25 min while optimum agitation time for banana stem and sugarcane bagasse were 200 min. All three agro-wastes adsorbents were able to performed best at an initial concentration of 70 mg/L. Due to the relatively high adsorption capacity of the dye, temperature of 60 °C is of interest for further application in treating dye.

Under the optimum conditions, all three agro-wastes adsorbents were able to remove more than 95 % of dye in the aqueous solution. As shown in Figure 4.7, kenaf was able to remove 67.87 mg/L of methylene blue while for banana stem and sugarcane bagasse, it was 68.47 mg/L and 68.19 mg/L, respectively.

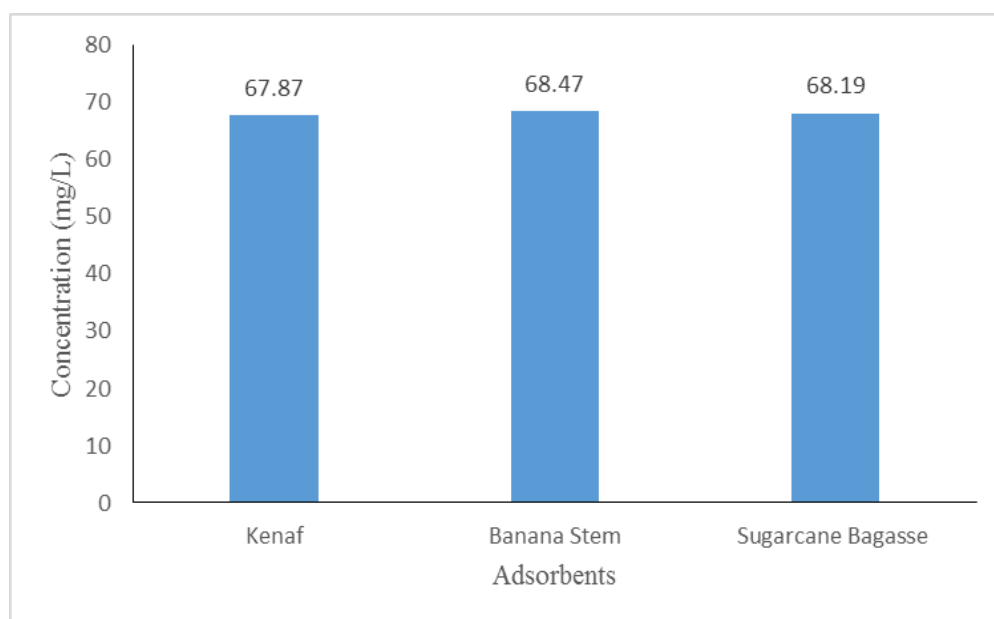


Figure 4.7: Maximum adsorption capacity of kenaf, banana stem and sugarcane bagasse.

#### 4.4 Isotherm Studies

##### 4.4.1 Langmuir Isotherm

Adsorption isotherms provides the capacity of the adsorbent and the equilibrium relationships between adsorbent and adsorbate that normally are the ratio between the quantity adsorbed and the remains in solution at fixed temperature at equilibrium (Igwe and Abia, 2007). Langmuir isotherm and Fruendlich isotherm are two simplest isotherms used to describe the adsorption behaviour by using adsorption equation (Igwe and Abia, 2007).

The experimental data from Table 4.5 did not fit the Langmuir isotherm as it give negative slopes and intercepts for all three adsorbents. Langmuir isotherm plots were shown in Figure 4.8, Figure 4.9 and Figure 4.10. All the graphs showed negative slopes and negative interceptions. Negative  $Q_m$  caused the actual adsorption value cannot be calculated.

Table 4.5: Langmuir isotherm constants and regression data for adsorption of methylene blue.

Adsorbents	Isotherm Constant	Temperature (K)		
		313K	333K	353K
Kenaf	$Q_m$ (mg/g)	-7.2254	-4.1563	-8.3126
	b (L/mg)	-0.1099	-0.1461	-0.0962
	$R^2$	0.9598	0.9252	0.9537
Banana stem	$Q_m$ (mg/g)	-7.4794	-8.3195	-8.058
	b (L/mg)	-0.1093	-0.1016	-0.1021
	$R^2$	0.7892	0.9623	0.9046
Sugarcane bagasse	$Q_m$ (mg/g)	-14.684	-5.9102	-17.301
	b (L/mg)	-0.0653	-0.1246	-0.0376
	$R^2$	0.9489	0.9858	0.9394

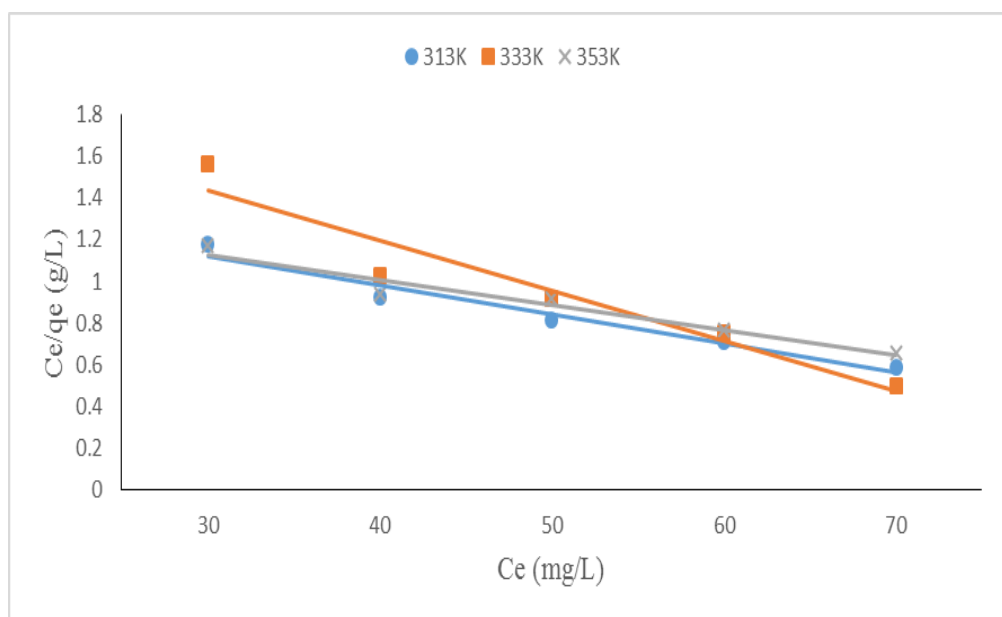


Figure 4.8: Langmuir plot for methylene blue dye by using kenaf.

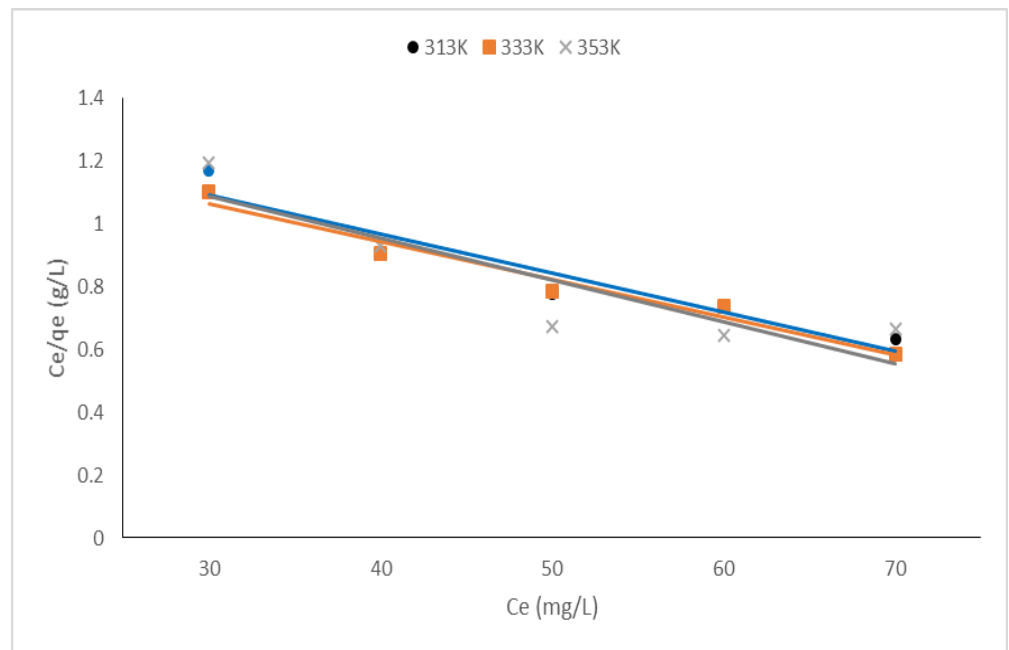


Figure 4.9: Langmuir plot for methylene blue dye by using banana stem.

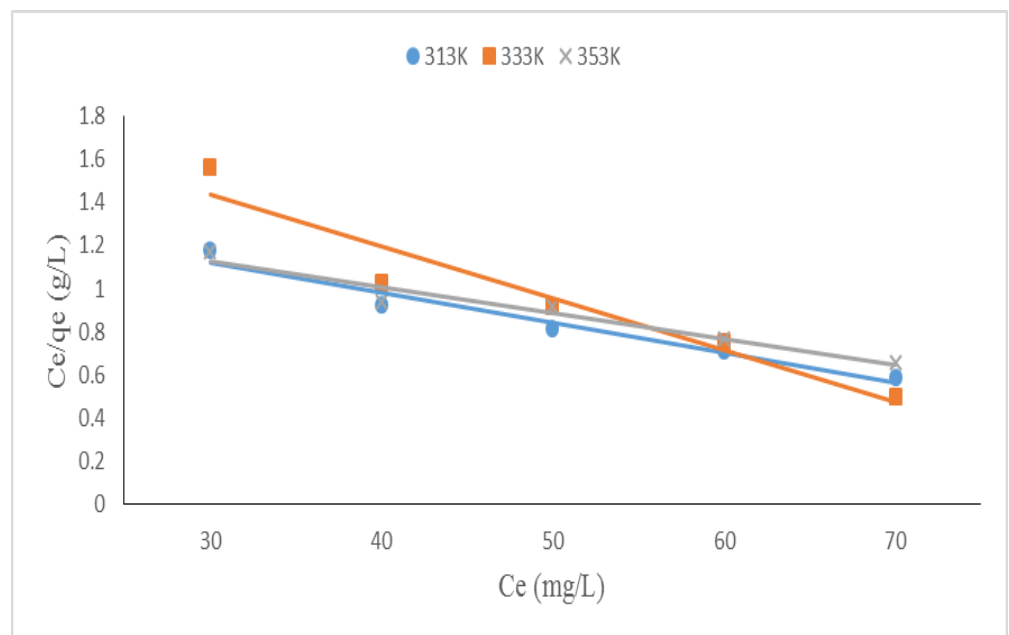


Figure 4.10: Langmuir plot for methylene blue by using sugarcane bagasse.

The Langmuir isotherm suggests that adsorbates are chemically adsorbed at a fixed number of well-defined sites in which each site can only hold one adsorbate species and all sites are generically equivalent (Prola *et al.*, 2013). This theory assume no interactions between the adsorbate species where the adsorption process occurs on a homogeneous surface to obtain maximum adsorption capacity (Prola *et al.*, 2013). This leads to a conclusion in which the adsorption behavior did not follow the assumptions according to Langmuir isotherm. Kiurski *et al.*, (2012) and Kiurski *et al.*, (2011) also showed similar results with negative slope and intercept of Langmuir isotherm.

#### **4.4.2 Freundlich Isotherm**

The Freundlich isotherm was found to fit the experimental data for methylene blue sufficiently in accordance with the linear correlations ( $R^2$ ). Freundlich isotherm model follow the principles where as the adsorbate concentration increases, the concentration of adsorbate on the surface will also increases. This model assumes the occurrence of an infinite amount of adsorption which is by having heterogeneous adsorption with different energy of active sites and eversible adsorption (Freundlich, 1906). The linear plot of Freundlich isotherms were shown in Figure 4.11, Figure 4.12 and Figure 4.13. All the graphs showed positive slopes and positive interceptions.

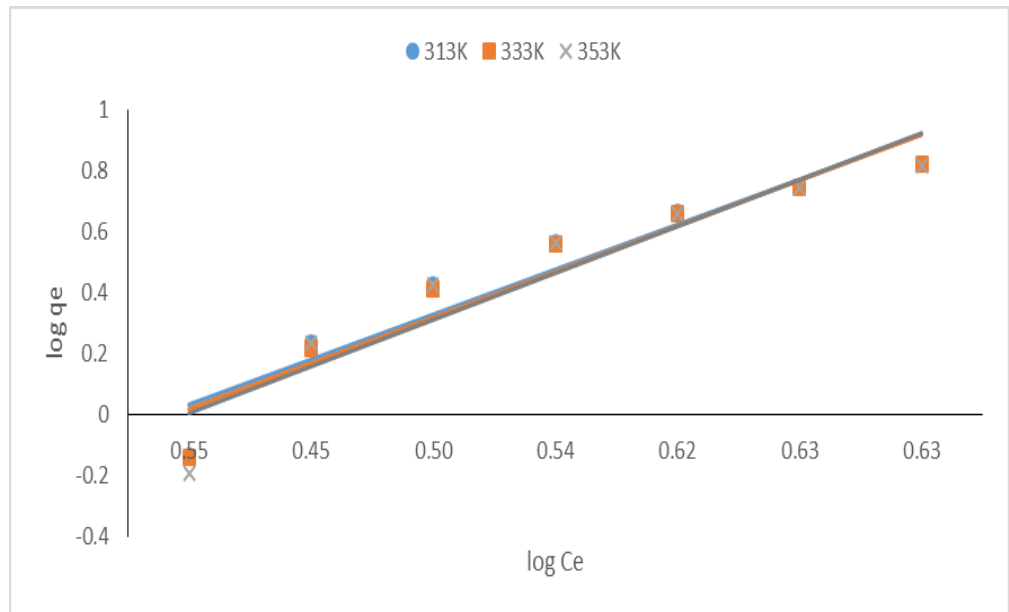


Figure 4.11: Freundlich plot for methylene blue using kenaf.

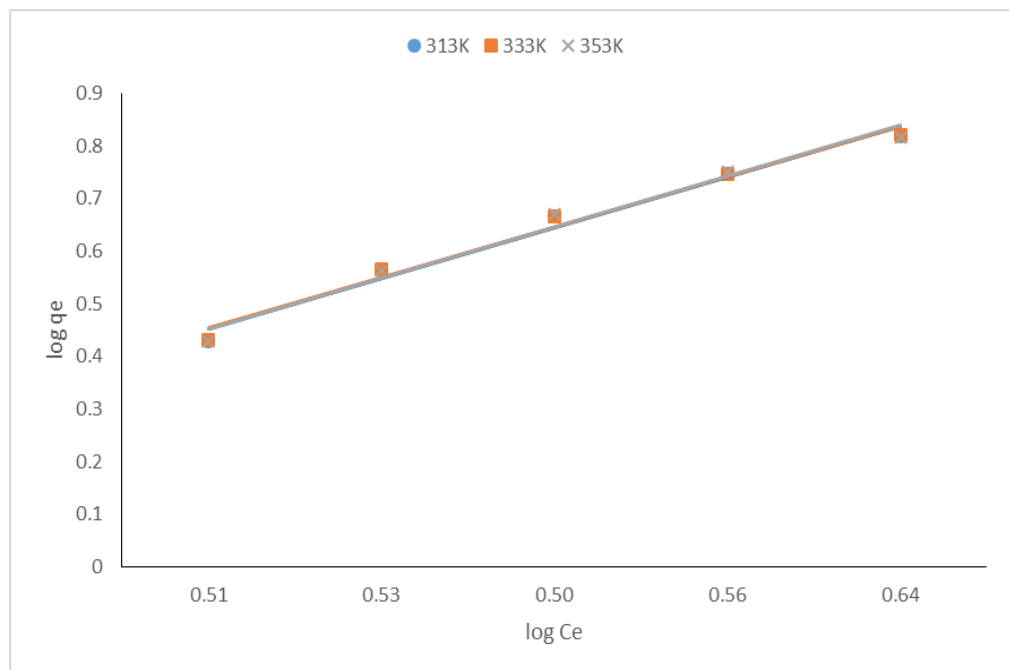


Figure 4.12: Freundlich plot of methylene blue using banana stem.



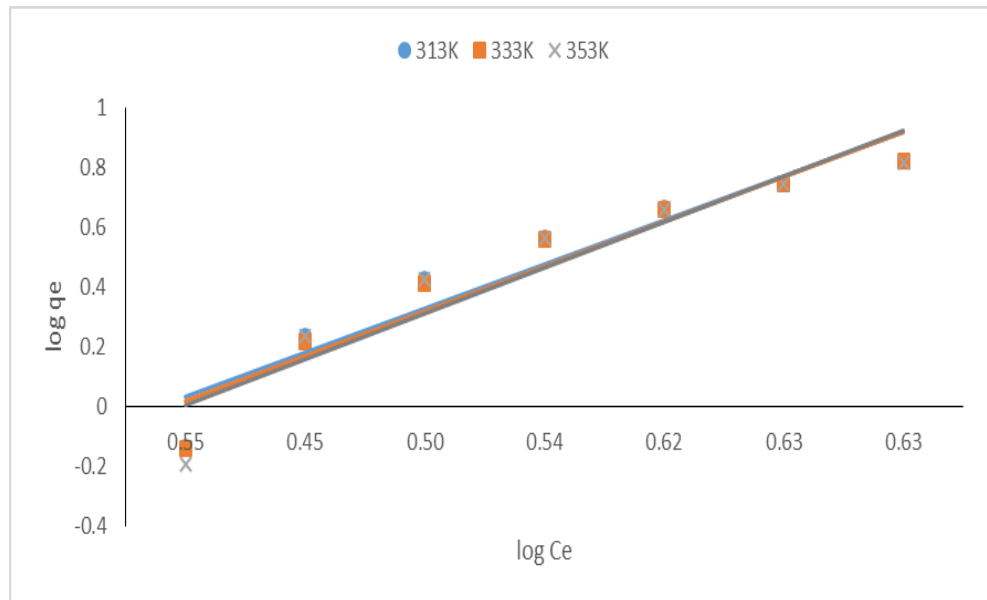


Figure 4.13: Freundlich plot of methylene blue using sugarcane bagasse.

The value of  $K_F$ ,  $n$  and regression correlation coefficients were calculated from the slope and intercept of these plots, and reported in Table 4.6.  $K_F((\text{mg/g})(\text{L/mh})^{1/n})$  indicates the relative adsorption capacity of the adsorbent related to bond energy where  $n$  is the heterogeneity factor representing the deviation from linearity of adsorption. If the  $n$  value is lower to unity, this shows that the adsorption process is chemical and if the value is above unity, this implies a favourable physical process (Aljebrori *et al.*, 2014). Hence, the adsorption process performed was a physical process. The  $R^2$  values of Freundlich isotherm at 333K (60°C) was the highest among all temperatures ( $R^2 = 0.9179$  (kenaf),  $R^2 = 0.9845$  (banana stem) and  $R^2 = 0.9863$  (sugarcane bagasse)). Based on  $K_F$  value, the adsorption equilibrium data fitted Freundlich isotherm model in the order of banana stem > sugarcane bagasse > kenaf.

Table 4.6: Freundlich isotherm constants and regression data for adsorption of methylene blue.

Adsorbents	Isotherm Constant	Temperature (K)		
		313K	333K	353K
Kenaf	$K_F$			
	$((\text{mg/g})(\text{L/mg})^{1/n})$	0.7679	0.7427	0.7168
	n	6.8027	6.6845	6.5488
	$R^2$	0.9087	0.9179	0.8893
Banana stem	$K_F$			
	$((\text{mg/g})(\text{L/mg})^{1/n})$	2.2735	2.2798	2.2745
	n	10.345	10.4167	10.3627
	$R^2$	0.9824	0.9845	0.9793
Sugarcane bagasse	$K_F$			
	$((\text{mg/g})(\text{L/mg})^{1/n})$	2.3094	2.2439	2.2111
	n	10.6496	10.2041	10.7066
	$R^2$	0.9861	0.9863	0.9839

#### 4.5 Adsorption Thermodynamic

Table 4.7: Thermodynamic parameters for kenaf, banana stem and sugarcane bagasse.

Samples	Temperature (K)	$\Delta G^\circ$ (kJ/mol)	$\Delta H^\circ$ (J/mol)	$\Delta S^\circ$ (J/K mol)
Kenaf	313	Negative	-0.43	3.72
	333	Negative		
	353	Negative		
Banana	313	Negative	-0.2	3.5
	333	Negative		
	353	Negative		
Sugarcane	313	Negative	-2.56	-3.01
	333	Negative		
	353	Positive		

Table 4.7 presents the thermodynamic parameters at various temperatures. Enthalpy of adsorption ( $\Delta H^\circ$ ), Gibb's free energy ( $\Delta G^\circ$ ) and entropy of adsorption ( $\Delta S^\circ$ ) for the determination of thermodynamics parameters are crucial as they contributes features on the final state of the system. Figure 4.14 show the van't Hoff plots in  $\ln K_d$  versus  $1/T$ . These parameters enable the justification whether the process is favourable under the thermodynamic point of view, the spontaneity of the system and if the adsorption process occurs with adsorption or release of energy (Vieira *et al.*, 2012).

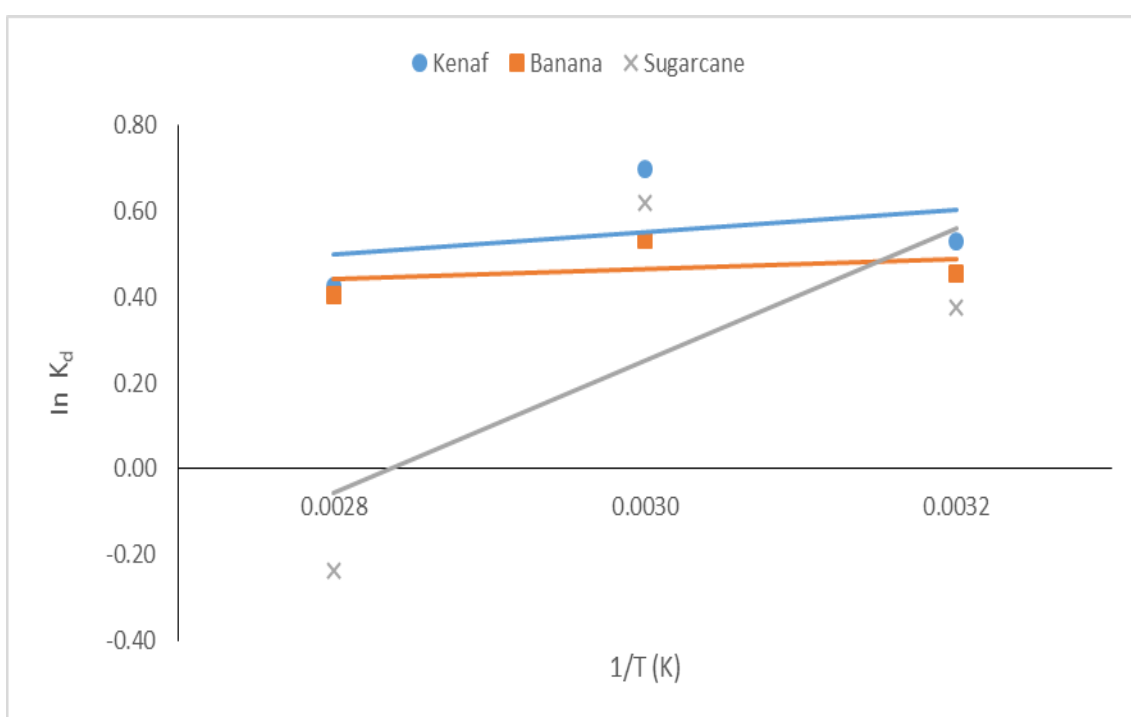


Figure 4.14: Van't Hoff plot for the estimation of thermodynamic parameters.

The negative values of  $\Delta G^\circ$  confirmed the spontaneity of methylene blue adsorption onto kenaf, banana stem and sugarcane bagasse. It also suggests that the process is thermodynamically feasible. Negative  $\Delta H^\circ$  proves the exothermic nature for the adsorption process. Positive value of  $\Delta S^\circ$  indicates good affinity of methylene blue towards adsorbents (kenaf and banana stem). Positive value of  $\Delta S^\circ$  showed an increased randomness at the solid/solution interface during methylene blue adsorption process

(Zhang *et al.*, 2011). Meanwhile, the negative value of  $\Delta S^\circ$  was caused by the lack of randomness at solid/solution interface (Muggundha *et al.*, 2013).

#### 4.6 Calorific Value

Calorific value is the heating value of a substance. Industrial sectors require a lot of combustion materials for combustion process. Combustion materials such as coal, charcoal and briquettes require high calorific value to ensure efficient and effective combustion. Hence, determination of calorific value is crucial. Table 4.8 shows the calorific value before and after the treatment for methylene blue removal. Experiment was conducted under optimum conditions (pH = pH 8, agitation time = 25 minutes (kenaf) and 200 minutes (banana stem and sugarcane bagasse), initial concentration = 70 mg/L and temperature = 60 °C).

Table 4.8: Calorific value before and after the treatment for kenaf, banana stem and sugarcane bagasse.

	Before treatment (Calories/gram)	After Treatment (Calories/gram)	Percentage of differences (%)
Kenaf	5418.76	7272.70	18.54
Banana Stem	4796.50	6689.66	18.93
Sugarcane bagasse	5517.11	9315.25	37.98

All of the three adsorbents showed an increase in calorific value after they were used to remove methylene blue dye from the wastewater. This might due to the presence of methylene blue dye molecules attached on the surface of the adsorbents. Sugarcane bagasse showed the highest calorific value after being used for ethylene blue removal which is 9315.25 calories/gram. Sugarcane bagasse showed a significant difference in calorific value of 3798.12 calories/gram before and after the methylene blue dye

removal. This might due to the advantage of sugarcane bagasse for its composition. The ascending sequence of calorific value for these three agro-wastes is sugarcane bagasse > kenaf > banana stem.

Higher calorific value proved to provide an advantage in combustion process. Hence, there is a potential to utilise all the three agro-waste adsorbents after their use for methylene blue dye removal in cement industry. As compared to commercialized agro wastes briquettes available, kenaf, banana stem and sugarcane bagasse exhibit higher calorific value. Table 4.9 showed the comparison of calorific value of agro wastes.

Table 4.9: Calorific value of agro wastes (AZEUS, 2012).

<b>Agro Wastes Briquettes</b>	<b>Cal./kg</b>
Groundnut shell*	4524
Palm kernel*	4985
Sawdust*	3898
Cotton stalks*	4252
Coffee husk*	4045
Tea waste*	4237
Paddy straw*	3469
Mustard stalk*	4200
Wheat straw*	4100
Sunflower stalk*	4300
Palm husk*	3900
Soya bean husk*	4170
Wood chips*	4785
Forestry waste*	3000
Banana Stem	6689.66
Sugarcane bagasse	9315.25
Kenaf	7272.70

\* references from AZEUS, 2012.

#### 4.7 Economic Feasibility

In this research, economic feasibility for three agro-wastes adsorbents were calculated. A rough assessment of the capital cost of kenaf, banana stem and sugarcane bagasse for dye was made based on the saturation capacity of the adsorbents alone without considering other factors such as regeneration or spent adsorbent disposal cost. The cost involved in using kenaf, banana stem and sugarcane bagasse as adsorbents is shown in Table 4.10.

Table 4.10: Cost of using kenaf, banana stem and sugarcane bagasse as adsorbents.

<b>Kenaf</b>		<b>Banana</b>	<b>Sugarcane</b>
Process	Charge (RM)	Charge (RM)	Charge (RM)
Agro-Waste (per kg) (National Kenaf and Tobacco Board, 2014)	1.70	FOC	FOC
Drying (Air Dry)	FOC	FOC	FOC
Grinding Process (1 hour x 7.5 Kw/h x 0.210)	1.60	1.60	1.60
Total (RM)	3.30	1.60	1.60

\*FOC = Free of charge

With reference to the cost, agro-wastes can be an effective option to reduce the cost of adsorbents. Although activated carbon is very effective in removing dye from aqueous solution, the high price of activated carbon in the market (approximately RM6548 per tonne) make the utilization of agro-wastes as adsorbents a good alternative.

Adsorption process showed many advantages as follow:

1. Easy to operate, convenience and simple in term of it's design (Bhatnagar and Minocha, 2006).
2. Low operational cost, easy automation, lack of sensitivity to toxic pollutants, high flexibility and potential of operation at low concentration, less investment of initial capital and environmental friendly (Auta and Hameed, 2013).
3. Low cost adsorbents (agro-waste adsorbents) used in this technique
4. Agro-waste adsorbents are abundance with potential adsorption capacity.
5. Low detrimental effect on treated water (Altaher, 2014).
6. Agro-based adsorbents are environmental friendly.
7. The use of agro-waste adsorbents can reduce the amount of wastes disposed in landfill.

## CHAPTER 5

### CONCLUSIONS

This study proves the potentials of some agro-waste to be utilized as low cost adsorbants for dye effluent. The results from this study shows that kenaf, banana stem and sugarcane bagasse exhibit more than 95% adsorption capacity at concentration of 70 mg/L methylene blue dye. The optimum parameters for the best adsorption capacity were achieved at pH 8, initial concentration of 70mg/l methylene blue and 60°C. The agitation time needed for kenaf was 25 minutes while for banana stem and sugarcane bagasse, it was 200 minutes.

Among all of the adsorbents, banana stem is the best in removing methylene blue dye as it can achieved maximum percentage (97.82%) of removal with an adsorption capacity of 68.48 mg/L. The results obtained are well fitted in the linear form of Freundlich adsorption isotherms. The calculated values of different thermodynamics parameters indicate that the ongoing adsorption process is feasible, spontaneous and exothermic in nature.

Based on the rough assessment of capital cost for agro-wastes production, the cost involved ranged between RM 1.60 to RM 3.30. As compared to activated carbon, agro-wastes as adsorbents are more economical. Besides, the calorific value of all the agro-wastes showed an increase in their calorific value after adsorption treatment process. Hence, it can be used as combustion materials for energy conversion in cement industry.



From the current research, it clearly proved that the use of agro-wastes (kenaf, banana stem and sugarcane bagasse) as adsorbent is economical, effective and more viable. It can efficiently be used to remove methylene blue dye.

## REFERENCES

- Abbasi, M. & Asl, N. R. (2008). Sonochemical degradation of Basic Blue 41 dye assisted by nanoTiO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>. *Journal of Hazardous Materials*, 153, 942–947.
- Abid, M. F., Zablouk, M. A. & Abid-Alameer, A. M. (2012). Experimental study of dye removal from industrial wastewater by membrane technologies of reverse osmosis and nanofiltration. *Iranian Journal of Environmental Health Science & Engineering*, 9, 17.
- Adams, C. D., Fusco, W. & Kanzelmeyer, T. (1995). Ozone, Hydrogen Peroxide/Ozone and UV/Ozone Treatment of Chromium and Copper Complex. Dyes: Decolorization and Metal Release. *Ozone Science & Engineering*, 17:149-161.
- Akbari, A., Remigy, J. C. & Aptel, P. (2002). Treatment of Textile Dye Effluent using a Polyamide-based Nanofiltration Membrane. *Chemical Engineering Procedure*, 41, 601-609.
- Aljebroori, A. M., Alshirifi, A. N. & Alkaim, A. F. (2014). Kinetics and equilibrium study for the adsorption of textile dyes onto coconut shell activated carbon. *Arabian Journal of Chemistry*, S1878-5352, 23-39.
- Altaher, H. (2014). Preliminary study of the effect of using biosorbents on the pollution of the treated water. *Global NEST Journal*, 16, 707-718.
- Altaher, H. & ElQada, E. (2011). Investigation of the treatment of colored water using efficient locally available adsorbent. *International Journal of Energy and Environment*, 2(6), 1113-1124.
- Amel, K., Hassena, M. A. & Kerroum, D. (2012). Isotherm and kinetics study of biosorption of cationic dye onto banana peel. *Energy Procedia*, 19, 286 – 295.
- Argun, M. E. (2010). Modification methods for the enhancement of adsorption capacity of adsorbents: a review. *International Journal of Environmental Application & Science*, 5(3), 463-469.
- Argun, M. E. & Dursun, S. (2008). A new approach to modification of natural adsorbent for heavy metal adsorption. *Biosource Technology*, 99, 2516-2527.
- Arslan, I., Balcioglu, I. A. & Bahnemann, D. W. (2000). Advanced chemical oxidation of reactive dyes in simulated dyehouse effluents by ferrioxalate-Fenton/UV-A and TiO<sub>2</sub>/UV-A processes. *Dyes Pigments*, 47, 207-218.
- Auta, M. & Hameed, B. H. (2013). Coalesced chitosan activated carbon composite for batch and fixed-bed adsorption of cationic and anionic dyes. *Colloids and Surface B: Biointerfaces*, 105, 199-206.

- AWWA Staff (2011). Operational control of coagulation and filtration processes (3<sup>rd</sup> ed.). United States: American Water works association.
- AZEUS Machinery. (2012). *Briquettes calorific value of common agro wastes*. Retrieved from: <http://charcoalbriquettemachine.com/briquettes-calorific-value/index.html>
- Baek, M. H., Ijagbemi, C. O., O, S. J. & Kim, D. S. (2010). Removal of malachite green from aqueous solution using degreased coffee bean. *Journal of Hazardous Materials*, 176, 820-828.
- Bansal, R. C. & Goyal, M. (2005). *Activated Carbon Adsorption*. Florida, United States: CRC Press.
- Bansal, R. C. & Goyal, M. (2005). *Activated carbon adsorption*. Boca Raton: Taylor & Francis.
- Bhatnagar, A & Minocha, A. K. (2006). Conventional and non-conventional adsorbents for removal of pollutants from water-A review. *Indian Journal of Chemical Technology*, 13, 203-217.
- Binnie, C., Kimber, M. & Smethurst, G. (2002). *Basic Water Treatment*. London, United Kingdom: Royal Society of Chemistry.
- Boumediene, M., Benaïssa, H., George, B., Molina, S. & Merlin, A. (2014). Characterization of two cellulosic waste materials (orange and almond peels) and their use for the removal of methylene blue from aqueous solutions. *Maderas-Cienc. Technology*, 17 (in press).
- Cencen, F & Aktas, O. (2011). *Activated carbon for water and wastewater treatment: Integration of adsorption and biological treatment*. Hoboken, New Jersey, United States: John Wiley & Sons.
- Chun, H. (2010). *A novel functionalized ordered mesoporous carbon as an efficient adsorbent for dye removal from water*. (Published Doctoral dissertation). The Hong Kong University of Science and Technology, Hong Kong.
- Ciardelli, G. & Ranieri, N. (2001). The treatment and reuse of wastewater in the textile industry by means of ozonation and electroflocculation. *Water Research*, 35, 567-572.
- Clark, M. (2011). *Handbook of Textile Dyeing: Principles, Processes and Types of Dyes*. Elsevier, 454.
- Cragan, J. D. (1999). Teratogen update: Methylene Blue. *Teratology*, 1, 42-48.
- Crini, G. (2006). Non-conventional low-cost adsorbents for dye removal: A review. *Bioresource Technology*, 97, 1061-1085.
- Deans, J. R. & Dixon, B. G. (1992). Uptake of Pb<sup>2+</sup> and Cu<sup>2+</sup> by novel biopolymers. *Water Research*, 26 (4), 469-472.

- Deng, H., Lu, J. J., Li, G. X., Zhang, G. L. & Wang, X. G. (2011). Adsorption of methylene blue on adsorbent materials produced from cotton stalk. *Chemical Engineering Journal*, 172, 326-334.
- Department of Statistics Malaysia. (2013). *Malaysia annual gross domestic product report 2005-2012*.
- Dotto, G.L., Vieira, M.L.G. & Pinto, L. A. (2012). Kinetics and Mechanism of Tartrazine Adsorption onto Chitin and Chitosan. *Industrial & Engineering Chemistry Research*, 51, 6862–6868.
- Easton, J. R. (1995). *Colour in Dyehouse Effluent*. The Alden Press Oxford, UK.
- Eckenfelder, W. W., Ford, D. L. & Englands, A. J. (2009). *Industrial water quality*. New York, NY: McGraw-Hill.
- Eglia, J. E. (2007). Wastewater treatment in the textile industry. *Pakistan Textile Journal*.
- Etim, U. J., Umoren, S. A. & Eduok, U. M. (2012). Coconut coir dust as a low cost Adsorbent for the removal of cationic dye from aqueous solution. *Journal of Saudi Chemical Society* (In press).
- Franca, A. S., Oliveira, L. S. & Nunes, A. A. (2010). Malachite green adsorption by residue-based microwave-activated adsorbent. *Clean-Soil Air Water*, 38(9), 843-849.
- Freundlich, H. (1906). Adsorption in solution. *The Journal of Physical Chemistry*, 40, 1361-1368.
- Gaehr, F., Hermanutz, F., & Oppermann, W. (1994). Ozonation - an important technique to comply with new German laws for textile wastewater treatment. *Water Science Technology*, 30, 255-263.
- Gaya, U.I. & Abdullah, A. H. (2008). Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: a review of fundamentals, progress and problems. *Journal of photochemistry and photobiology C*, 9,1-12.
- Ghayeni, S. B., Beatson, P. J., Schneider, R. P. & Fane, A. G. (1998). Water reclamation from municipal wastewater using combined microfiltration-reverse osmosis (MERO. Preliminary performance data and microbiological aspects of system operation. *Desalination*, 116, 65-80.
- Gupta, V. K. & Suhas. (2009). Application of low-cost adsorbents for dye removal – A review. *Journal of Environmental Management*, 90, 2313-2342.
- Hamdaoui, O. (2006). Batch study of liquid-phase adsorption of methylene blue using cedar sawdust and crushed brick. *Journal of Hazardous Materials*, B135, 264-273.

- Hamzeh, Y., Ashori, A., Azadeh, E., Abdulkhani, A. (2012). Removal of Acid Orange 7 and Remazol Black 5 reactive dyes from aqueous solutions using a novel biosorbent. *Materials Science and Engineering*, 132, 1394-1400.
- Han, R., Wang, Y., Yu, W., Zou, W., Shi, J. & Liu, H. (2007). Biosorption of methylene blue from aqueous solution by rice husk in a fixed-bed column. *Journal of Hazardous Materials*, 141, 713-718.
- Han, R., Zhang, L., Song, C., Zhang, M., Zhu, H., & Zhang, L. (2010). Characterization of modified wheat straw, kinetic and equilibrium study about copper ion and methylene blue adsorption in batch mode. *Carbohydrate Polymers*, 79(4), 1140-1149.
- Han, X., Wang, W. & Ma, X. (2011). Adsorption characteristics of methylene blue onto low cost biomass material lotus leaf. *Chemical Engineering Journal*, 171, 1-8.
- Hasnain, I. M., Lee, S. L., Faridah, A. H., Aziza, H. A., Ramlia, N. A. & Dhase, J. P. A. (2007). Low cost removal of disperse dyes from aqueous solution using palm ash. *Dyes and Pigments*, 74 (2), 446–453.
- Hilal, N. M., Ahmed, I. A. & Badr, E. E. (2012). Removal of acid dye (AR37) by adsorption onto potatoes and egg husk: a comparative study. *The Journal of American Science*, 8, 341-348.
- Igwe, J. C. & Abia, A. A. (2007). Adsorption isotherm studies of Cd (II), Pb (II) and Zn (II) ions bioremediation from aqueous solution using unmodified and EDTA-modified maize cob. *Eclética Química*, 32, 33-42.
- Jayarajan, M., Arunachalam, R. & Annadurai, G. (2011). Use of low cost nano-porous materials of pomelo fruit peel wastes in removal of textile dye. *Research Journal of Environmental Sciences*, 5 (5), 434-443.
- Karmakar, S. R. (1999). *Chemical Technology in the Pre-treatment Process of Textiles. Textile Science and Technology. Elsevier science*. Retrieved from <http://www.scribd.com/doc/23550955/CHEMICAL-TECHNOLOGY-IN-THE-PRE-TREATMENT-PROCESSES-OF-TEXTILES.pdf>
- Kelesoğlu, S. (2007). Comparative adsorption studies of heavy metal ions on chitin and chitosan biopolymers. (Published Master degree's thesis). Izmir Institute of Technology, Turkey.
- Khataee, A.R., Vafaei, F. & Jannatkhan, M. (2013). Biosorption of three textile dyes from contaminated water by filamentous green algal *Spirogyra* sp.: Kinetic, isotherm and thermodynamic studies. *International Bioremediation & Biodegradation*, 83, 33-40.
- Khatod, I. (2013). Removal of Methylene Blue dye from aqueous solutions by neem leaf and orange peels powder. *International Journal Chemical Technology Resource*, 5, 572-577.

- Khattari, S.D. & Singh, M.K. (2009). Removal of malachite green from dye wastewater using neem sawdust by adsorption. *Journal of Hazardous Materials*, 167, 1089-1094.
- Kiueski, J., Adamovic, S., Krstic, J., Oros, I. & Miloradov, M. V. (2011). Adsorption efficiency of low-cost materials in the removal of Zn (II) ions from printing developer, *Acta technical corviniensis-Bulletin of engineering, Romania*.
- Kiurski, J., Adamovic, S., Oros, I., Krstic, J. & Kovacevic, I.(2012). Adsorption feasibility in the Cr (total) ions removal from waste printing developer. *Global NEST Journal*, 14, 18-23.
- Kucera, J (2011). *Reverse Osmosis: Design, Processes, and Applications for Engineers*. John Wiley & Sons, 1.
- Lam, F.L.Y. (2005). *Development of MCM-41 based catalysts for the photo-fenton's degradation of dye pollutants*. (Published Phd's thesis). University of Science and Technology, Hong Kong.
- Lawrence, K. W., Chen, J. P., Hung, Y. T. & Shammas, N. K. (2010). *Membrane and Desalination technologies*. Springer Science & Business Media.
- Ledakowicz, S., Solecka, M. & Zylla, R. (2001). Biodegradation decolourisation and detoxification of textile wastewater enhanced by advanced oxidation processes. *Journal. Biotechnology*, 89, 175-184.
- Lee, S. M. (2009). *Removal of Basic Dye from Aqueous solution by adsorption onto palm oil ash*. (Unpublished Master's Thesis). University of Malaya, Kuala Lumpur.
- Lee, K. L., Udin, Z. M. & Hassan, M. G. (2014). Global supply chain capabilities in Malaysian textile and apparel industry. *International Journal of Supply Chain Management*, 3, 2, 31-40.
- Lim, S. H. (2011). *Remediation of Industry Wastewater Effluent by Using Kenaf As Waxes Absorbent*. (Bachelor Degree's Thesis).University Malaysia Kelantan, Kelantan.
- Lin, S. H. & Chen, M. L. (1997). Treatment of Textile Wastewater by Chemical Methods for Reuse. *Water Research*, 31, 868-876.
- Lowell, S., Shields, J. E., Thomas, M. A. & Thommes, M. (2004). *Characterization of porous solids and powders: surface area, pore size and dentistry, Dordrecht*. Boston, MA: Kluwer Academic Publishers.
- Mahmoued, E. K. (2010). Cement kiln dust and coal filters treatment of textile industrial effluents. *Desalination*, 255, 175 – 178.
- Malaysian Investment Development Authority. (2012). Industries in Malaysia: Textiles and Apparels Industry. Retrieved from: <http://www.mida.gov.my/env3/index.php?page=textiles-and-apparel-industry>

- Malaysian Knitting Manufacturers Association. (1998). Statistics of Malaysian Textile Industry. Retrieved from: <http://www.sabah.edu.my/fan/stats1.htm>
- Malaysian Knitting Manufacturers Association (2014). Malaysian exports of textile and apparel by year. Retrieved from <http://www.mkma.org/statistic/2015/2014ExportbyYear.htm>.
- Mitchell, M. M. (2006). *Textile and apparel exports boost Malaysia's economy and are key to its industry's future*. Retrieved from: [http://www.textileworldasia.com/Articles/2006/September/October/Features/Malaysia\\_Textile\\_Industry\\_Profile.html](http://www.textileworldasia.com/Articles/2006/September/October/Features/Malaysia_Textile_Industry_Profile.html)
- Mitchell, M. M. (2006). Textile and apparel exports boost Malaysia's economy and are key to its industry's future. *Textile World Asia*. Retrieved from: [http://www.textileworldasia.com/Issues/2006/September/October/Features/Malaysia-Textile\\_Industry\\_Profile](http://www.textileworldasia.com/Issues/2006/September/October/Features/Malaysia-Textile_Industry_Profile)
- Mobarekeh, M. N. (2007). *Isotherm and Kinetics of Reactive Dye Adsorption on Palm Kernel Shell-Based Activated Carbon*. (Master's Thesis). University Putra Malaysia, Serdang.
- Mohammad, A. W., Teow, Y. H., Ang, W. L., Chug, Y. T., Oatley-Radcliffe, D. L. & Hilal, N. (2014). Nanofiltration membranes review: recent advances and future prospects. *Desalination*.
- Moubarak, F., Atmani, R., Maghri, I., Elkouali, M., Talbi, M. & Latifa, M. (2014). Elimination of Methylene Blue dye with natural adsorbent "banana peels powder". *Global Journal of Science Frontier Research*, 14, 39-44.
- Muggundha, R., Sharifah, M. & Mohd, R. A. (2013). Removal of 2,4-dichlorophenol using cyclodextrin-ionic liquidpolymer as a macroporous material: Characterization, adsorptionisotherm, kinetic study, thermodynamics. *Journal of Hazardous Materials*, 263, 501-516.
- Naba, T. N. (2014). *Characterization of nanofiltration membranes for sulphate rejection*. (Published PhD's Thesis). University of Glasgow, Scotland, United Kingdom.
- Namasivayam, C. & Sumithra, S. (2005). Removal of direct red 12B and methylene blue from water by adsorption onto Fe(III)/Cr(III) hydroxide, an industrial solid waste. *Journal of Hazardous Material*, B92, 263 – 274.
- Nasuha, N., Hameed, B. H. & Din, A. T. M. (2010). Rejected tea as a potential low-cost adsorbent for the removal of methylene blue. *Journal of Hazardous Mater*, 175(1-3), 126-132.
- Nataraj, S. K., Hosamani, K. M. & Aminabhavi, T. M. (2009). Nanofiltration and reverse osmosis thin film composite membrane module for the removal of dye and salts from the simulated mixtures. *Desalination*, 249, 1, 12-17.

- Njoku, V. O., Foo, K. Y., Asrif, M. & Hameed, B. H. (2014) Preparation of activated carbons from rambutan (*Nephelium lappaceum*) peel by microwave-induced KOH activation for acid yellow 17 dye adsorption. *Chemical Engineering Journal*, 250, 198–204.
- Noreen, S., Bhatti, H. N., Nausheen, S., Sadaf, S. & Ashfaq, M. (2013). Batch and fixed bed adsorption study for the removal of Drimarine Black CL-B dye from aqueous solution using a lignocellulosic waste: A cost effective adsorbent. *Industrial Crops and Products*, 50, 568 – 579.
- Öktem, Y. A., Pozan Soylu, G. S. & Aytan, N. (2012). The adsorption of Methylene Blue from aqueous solution by using waste potato peels: equilibrium and kinetic studies. *Journal of Science Industrial Resource*, 71, 817-821.
- Ong, S. T., Khoo, E. C., Hii, S. L. & Ha, S. T. (2010). Utilization of sugarcane bagasse for removal of basic dyes from aqueous environment in single and binary systems. *Desalination water treatment*, 20(1-3), 86-95.
- Ozacar, M. & Sengil, A. I. (2003). Adsorption of reactive dyes on calcined alunite from aqueous solutions. *Journal of Hazardous Materials*, 98, 211–224.
- Pala, A. & Tokat, E. (2002). Color removal from cotton textile industry wastewater in an activated sludge system with various additives. *Water Research*, 36, 2920-2925.
- Pathiraja, I. K. (2014). *Removal of acid yellow 25 dye onto chitin extracted from waste crab legs and study of adsorption isotherms and kinetics of AY25 dye adsorption*. (Published master's thesis). Southern Illinois University, Edwardsville.
- Paven, F. A., Gushikem, Y., Mazzocato, A. C., Dias, S. L. P. & Lima, E. C. (2007). Statistical design of experiments as a tool for optimizing the batch conditions to methylene blue biosorption on yellow passion fruit and mandarin peels. *Journal of Dyes and Pigments*, 72, 256-266.
- Pavan, F. A., Mazzocato, A. C. & Gushikem, Y. (2008). Removal of methylene blue dye from aqueous solutions by adsorption using yellow passion fruit peel as adsorbent. *Bioresource Technology*, 99, 3162-3165.
- Pearce, C. I., Lloyd, J. R. & Guthrie, J. T. (2003). The removal of colour from textile wastewater using whole bacterial cells: a review. *Dyes and Pigments*, 58(3), 179-196.
- Pereira, L. & Alves, M. (2012). Dyes - Environmental Impact and remediation. Malik, A. & Grohmann, E. Environmental Protection Strategies for Sustainable Development. Springer Dordrecht London, New York, 122.
- Pignon, H. M., Faur, C & Cloirec, P. L. (2006). Adsorption of dyes onto activated carbon cloth: Using QSPRs as tools to approach adsorption mechanisms. *Chemosphere*, 66 (2007) 887–893.



- Pizzi, N. G. (2011). *Water Treatment Operator Handbook*. America: American Water Works Association.
- Price, A., Cohen, A. , & Johnson, I. (2005). J.J. Pizzuto's fabric science. *New York: Fairchild Publications*.
- Prola, L .D. T. , Acayanka, E., Lima, E. C., Umpierres, C. S., Vaghetti, J. C. P., Santos, W. O., Laminsi, S. & Djifon, P. T. (2013) Comparison of *Jatropha curcas* shells in natural form and treated by non-thermal plasma as biosorbents for removal of reactive red 120 textile dye from aqueous solution. *Industrial Crops and Products*, 46, 328-340.
- Rangabhashiyam, S., Anu. N., & Selvaraju, N. (2013). Sequestration of dye from textile industry wastewater using agricultural waste products as adsorbents. *Journal of Environmental Chemical Engineering*, 1, 629-641.
- Seong, L. W. (2007). Malaysian textile & apparel industry. *Penang Economic Monthly*, 9, 1-28.
- Sentruk, H. B., Ozdes, D. & Duran, C. (2010). Biosorption of Rhodamine 6G from aqueous solutions onto almond shell (*Prunus dulcis*) as a low cost biosorbent. *Desalination*, 252, 81-87.
- Sharifah Nhatasha Syed Jaafar (2006). *Adsorption study – dye removal using clay*. University College of Engineering & Technology Malaysia, Pahang.
- Shertate, R.S. & Thorat, P.R. (2013). Biotransformation of a Textile AZO Dye Acid Yellow 25 by *Marinobacter Gudaonensis* AY-13. *Journal of Engineering, Computers & Applied Sciences (JEC&AS)*, 2, 4, 35-45.
- Sohrabi, M. R. & Ghavami, M. (2008). Photocatalytic degradation of Direct Red 23 dye using UV/TiO<sub>2</sub>: effect of operational parameters. *Journal of Hazard. Mater*, 153, 1235–1239.
- Somasekhara Reddy, M. C., Sivaramakrishna, L. & Varada Reddy, A. (2012). The use of an agricultural waste material, Jujuba seeds for the removal of anionic dye (Congo red) from aqueous medium. *Journal of Hazardous Materials*, 203–204, 118–127.
- Sleiman, M., Vildoza, D. L., Ferronato, C., Chovelon, J. M. (2007). Photocatalytic degradation of azo dye Metanil Yellow: optimization and kinetic modeling using a chemometric approach. *Applied. Catalysis*, B 77, 1–11.
- Sudarjanto, G., Lehmann, B. K. & Keller, J. (2006). Optimization of integrated chemical–biological degradation of a reactive azo dye using response surface methodology. *Journal of Hazard. Mater*, 160–168.
- Tiong, K.G. (2013). Identification of kenaf (KB-6) potential as industrial absorbent. (Unpublished degree's thesis). University Malaysia Kelantan, Kelantan.

- Torres, J. M. O., Cardenas, C. V., Moron, L. S., Guzman, A. P. & Cruz, T. E. E. (2009). Dye decolorization activities of marine-derived fungi isolated from Manila Bay and Calatagan Bay, Philippines. *Philippine Journal of Science*, 140 (2): 133-143.
- Vieira, S. S., Magriotis, Z. M., Santos, N. A. V., Cardoso, M. D. G. & Saczk, A. A. (2011). Macauba palm (*Acrocomia aculeate*) cake from biodiesel processing: An efficient and low cost substrate for the adsorption of dyes. *Chemical Engineering Journal*, 183, 152-161.
- Worch, E. (2012). *Adsorption technology in water treatment: Fundamentals, processes and modelling*. Berlin, Germany: Walter de Gruyter.
- Wu, J. S., Liu, C. H., Chu, K. H. & Suen, S. Y. (2008). Removal of cationic dye methyl violet 2B from water by cation exchange membranes. *Journal of Membrane Science*, 309, 239–245.
- Xing, Y., Liu, D. & Zhang, L. P. (2010). Enhanced adsorption of Methylene blue by EDTAD-modified sugarcane bagasse and photocatalytic regeneration of the absorbent. *Desalination*, 259, 187-191.
- Yagub, M. T., Sen, T. K., Afroze, S. & Ang, H. M. (2014). Dye and its removal from aqueous solution by adsorption: A review. *Advances in colloid and interface science*, 209, 172-184.
- Yang, R.T. (2003). *Adsorbents: fundamentals and applications*. Hoboken, N.J: Wiley-Interscience, John Wiley & Sons, Inc.
- Yasmin, C. M. (2004). *Adsorption Studies of Dyes using Clay-Based and Activated Carbon Adsorbents*. (Master's Thesis). University Sains Malaysia, Pulau Pinang.
- Yousif, B. F., Shalwan, A., Chin, C. W. & Ming, K. C. (2012). Flexural properties of treated and untreated kenaf/ epoxy composites. *Materials and Design*, 40, 378-385.
- Zaghbani, N., Hafiane, A. & Dhahbi, M. (2008). Removal of Safranin T from wastewater using micellar enhanced ultrafiltration. *Desalination*, 222, 348–356.
- Zhang, H., Tang, Y., Xianan, L., Ke, Z., Su, X., Cai, D., ... Yu, Z. (2011). Improved adsorptive capacity of pine wood decayed by fungi *Poria cocs* for removal of malachite green from aqueous solution. *Desalination*, 274, 97-104.

## **LIST OF PUBLICATIONS AND PAPERS PRESENTED**

19<sup>TH</sup> Biological Science Graduate Congress Singapore (19<sup>th</sup> BSGC Singapore)  
Adsorption Studies of Methylene Blue on Banana Stem  
Poster Presentation